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Available sulfur in some Iowa soils

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AVAILABLE SULFUR IN SOME IOWA SOILS

by

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INTRODUCTION

The essentiality of sulfur for plant growth has been known from the time of Liebig, but compared with other major nutrients such as nitrogen, phosphorus and potassium it has, until recently, received little attention. In many areas, soils contain insufficient available sulfur for the growth of economic crops and the sulfur needs have been met by the use of superphosphate, applied essentially to correct phosphate deficiency. Atmospheric sources have also contributed sufficient sulfur for crop needs in such industrialized areas as Western Europe or the eastern part of the United States. Whitehead (1964) has suggested that where more than 10 lb. S per acre per year is carried down in precipitation, sulfur deficiency is unlikely to occur. In many irrigated areas irrigation water has been an excellent source of sulfur.

Sulfur deficiency has been reported with increasing frequency in many parts of the world in recent years, and it has been predicted (Coleman, 1966) that a much larger area will become increasingly sulfur deficient in the future. Factors contributing to this trend, according to Coleman (1966) are:

1. Increasing use of sulfur-free fertilizers.
2. Increasing crop yields which make greater demands on soil nutrients.

3. Decreasing returns of sulfur from the atmosphere as a result of less combustion of coal and other sulfur-containing fuels and the implementation of air pollution control schemes.
4. Decreased use of sulfur-containing fungicides and insecticides.

In the United States significant responses to sulfur have been reported in most western and southeastern states (Jordon and Reisenauer, 1957). In the Midwest it has been generally accepted that soils are well supplied with sulfur. The studies of Evans and Rost (1945) on Minnesota soils indicated that total sulfur, which contained up to 75 percent organic S, was closely related to total carbon and nitrogen in the soil. Because many of the chernozems and brunizems examined were well supplied with organic carbon and nitrogen, it was inferred that the sulfur supply for plant growth would therefore be adequate.

In a recent review Beaton (1969) indicates that crop responses to applied sulfur have been reported in Iowa, Kansas, Minnesota, Nebraska and Wisconsin and that these responses have been associated mainly with coarse-textured soils. In Iowa, Brown and Kellogg (1915) were first to investigate the sulfur status of some representative soils. They determined both total sulfur and water soluble sulfate and concluded that Iowa soils contained inadequate levels

of total sulfur. The criterion of an adequate level of total sulfur was based on the assumption that the soil should contain as much total sulfur as it does total phosphorus. Apparently the total sulfur levels found were lower than those of total phosphorus. Later Erdman (1923) and Erdman and Bollen (1925) conducted field experiments with gypsum on soils in northcentral and northeast Iowa, and obtained some large responses with alfalfa and small ones with oats and red clover. Responses to gypsum were not obtained when applied to corn. No attempt was made by these workers to relate available sulfur in soil with crop response to applied sulfur.

Much progress has been made in Iowa since the 1920's in relating soil fertility to crop growth, but there is little information as yet concerning available sulfur in Iowa soils and its relationship to crop growth. As crop yields continue to increase, in response to improved varieties, heavier fertilization and better cultural practices, so will the sulfur requirements of the crop increase. It is essential, therefore, that studies be undertaken to provide basic information on the sulfate status of Iowa soils and to develop a soil test that will provide an index of plant-available sulfur. The research reported in this dissertation was initiated to obtain information in this general area. More specifically, the objects of this

research were:

1. To evaluate the available sulfur status of some representative Iowa soils by correlation of sulfur extracted chemically with sulfur taken up by ryegrass under greenhouse conditions.
2. To study the availability of applied sulfate to ryegrass on a range of Iowa soils and to assess the effect of air-drying on the availability of sulfur in these soils.
3. To study the distribution of available sulfur with depth and time in some representative soil profiles.

REVIEW OF LITERATURE

Sulfur is an essential nutrient for both plant and animal life and the biological transformations of sulfur resemble those of nitrogen. It can exist in a number of oxidation states which enable it to undergo many diverse reactions and to form a wide range of both organic and inorganic compounds. Oxidation numbers representative of sulfur in various oxidation states are: sulfate, +6; sulfite, +4; thiosulfate, +6 and -2; elemental S, 0; disulfite, -1 and sulfide, -2.

Plants play a major role in the conversion of inorganic sulfate to organic sulfur compounds in soil. Plants take up sulfur as the sulfate ion, which on reduction is elaborated into a number of organic compounds. Of these, the amino acids, methionine and cysteine, the primary products of sulfur metabolism in plants, comprise about 90 percent of the total sulfur. When plant residues are returned to the soil, microorganisms utilize part of the sulfur released from organic sulfur for their own cell synthesis, and only sulfur in excess of their requirements, is released for plant growth (Freney, 1967). Much of the sulfur added to soil in plant residues will remain as part of the soil humus. Transformations of this kind have been demonstrated by Scharpenseel and Krausse (1963) who showed that humic acid preparations from soils, to which plant residues containing

S^{35} had been added, indicated high labeling in the methionine but not the cystine fraction.

Oxidation-reduction reactions involving sulfur are important in soil systems. Under aerobic conditions, microorganisms transform sulfur compounds to sulfate. Some of the organic sulfur may be released as incompletely oxidized inorganic sulfur compounds such as sulfide, elemental S, thiosulfate and tetrathionate but studies by Starkey (1964) show that complete conversion to sulfate occurs quite rapidly.

Under anaerobic conditions sulfates are reduced to sulfides by microorganisms, mainly by bacteria of the genus Desulfovibrio. The mechanism of H_2S formation from sulfate according to Alexander (1961), involves a stepwise reduction via sulfite, sulfoxylate and sulfur hydrate. Decomposition of organic sulfur compounds under anaerobic conditions will result in an accumulation of mercaptans and hydrogen sulfide (Takai and Asami, 1962). Reducing conditions are not essential however, for the formation of mercaptans. In the aerobic decomposition of methionine in soil, de Barjac (1952) obtained initially, a considerable release of mercaptans, which in time were oxidized to sulfite and sulfate.

In surface soils of humid regions the amount of inorganic sulfur present at any one time is small in relation to the total sulfur content (Ensminger, 1954; Freney,

1961; Neller, 1959; Williams and Steinbergs, 1959). Most of the total sulfur is present in organic combination and mineralization of these organic forms is believed to be an important source of available sulfur. In drier regions, sulfur may accumulate as gypsum within the soil profile or occur as co-precipitated or co-crystallized sulfate associated with calcium carbonate in calcareous soils (Williams and Steinbergs, 1959; Williams et al., 1960). Williams and Steinbergs (1959) found that inorganic sulfate accounted for, on the average, two-thirds of the total sulfur in calcareous soils.

Recent reviews dealing with available sulfur in soil (Jordon and Ensminger, 1958; Freney et al., 1962; Whitehead, 1964; and Reisenauer, 1967) indicate an increased awareness of the practical significance of sulfur for crop growth. This review of literature will consider forms of available sulfur in soil, factors affecting the levels of available sulfur, methods of determining available sulfur, and evaluation of these methods. Because the availability of sulfur is dependent on mineralization of organic sulfur, some discussion of the various fractions of total soil sulfur is considered pertinent to this review.

Forms of Sulfur in Soils

Organic sulfur

The total sulfur content of most mineral soils has been found to lie between 0.01 and 0.05 percent (Whitehead, 1964), while for organic soils up to 0.5 percent sulfur may be present. The major part of the total sulfur of surface soils in humid regions occurs in organic combination, whereas in lower horizons inorganic sulfur appears to predominate (Evans and Rost, 1945; Walker and Adams, 1958; Bardsley and Lancaster, 1960; Aidinyan, 1964). Most of these studies indicate that organic S constitutes more than 90 percent of the total soil S in humid regions, whereas the analyses of Evans and Rost (1945) for Minnesota soils indicate maximum values of 75 percent. Because H_2O_2 was used to oxidize organic S to sulfate, the low values they obtained could have resulted from volatilization of certain organic S compounds, as suggested by Bardsley and Lancaster (1960), or by incomplete oxidation to sulfate of some organic S compounds. Evans and Rost (1945) also showed large differences between Great Soil Groups in the percentage of total S in organic form. For example, chernozems and black prairie soils were found to contain a much greater fraction as organic S than podsols.

While total organic S in soil is frequently measured, the identity of the constituent organic sulfur compounds

is not well known. Broadly, soil organic sulfur can be divided into two fractions, carbon-bonded sulfur (C-S), and noncarbon-bonded sulfur such as ester sulfates $R\text{-}O\text{-}SO_3$. Methods for the determination of organic sulfur in soil have been summarized recently by Beaton, Burns and Platou (1968).

Carbon-bonded sulfur is determined by the reduction of organic S to H_2S with Raney nickel (Lowe and DeLong, 1963) Arkley (1961) considered the more important linkages in the carbon-bonded sulfur group to be disulfide, sulfhydryl, sulfoxide, sulfinic acid, sulfone and sulfonic acid. The carbon-bonded sulfur includes the amino acids, cystine and methionine. In Alberta soils, Lowe (1966) has found that amino acid sulfur accounted for 39 percent of the total carbon-bonded fraction. In mineral soils, Lowe and DeLong (1963) found that carbon-bonded sulfur amounted to 12 to 35 percent of total organic and inorganic sulfur compared with 47 to 50 percent in organic soils.

In the noncarbon-bonded fraction of organic sulfur, a significant portion is considered to be in covalent sulfate groups in ester linkages (Freney, 1961). These organic sulfates--phenolic sulfates, choline sulfates and sulfate esters of carbohydrates can be extracted by digestion with a reducing mixture (hydriodic, formic and hypophosphorus acid), which converts SO_4 to H_2S. The amount of H_2S formed

is then estimated as methylene blue according to Johnson and Nishita (1952). This fraction is referred to as "HI-reducible" sulfur and contains, besides organic sulfates, inorganic sulfur of which sulfate is the dominant form (Lowe, 1966). Estimates of the organic sulfate contents of soils suggest that an average 52 percent of the total S is in this form (Freney, 1961; Lowe, 1964; Lowe and DeLong, 1963).

Inorganic sulfur

In well-drained, arable soils, almost all the inorganic sulfur occurs as the sulfate ion in combination with cations such as calcium, magnesium, potassium or ammonium. This sulfate may be associated with these cations in the soil solution or precipitated as salts of these elements in arid soils, or the sulfate may be adsorbed by 1:1 clays and hydrous oxides of iron and aluminum. Reduced forms of inorganic sulfur, such as sulfides and polysulfides, normally are not found in well-drained, upland soils, but occur mainly under reducing conditions caused by poor drainage or submergence. Because they are not a component of normal well-drained soils they will not be considered further in this review.

According to Harward and Reisenauer (1966), inorganic sulfate normally accounts for less than 10 percent of the total sulfur in surface soils, but in subsoils may represent a large proportion of the total. Soluble sulfate in the soil solution is in equilibrium with the solid phase forms, both

that adsorbed on the sequioxides in acid soils, and that present as slightly soluble compounds in soils of arid regions. Reisenauer (1967) states that ". . . it is these soluble forms, their amount, rate of renewal, distribution within and losses from the rooting zone that dominate the nutritional status of a crop."

Inorganic sulfate in soil has been divided into two components, a water soluble fraction extractable by neutral salt solutions such as 0.15 percent $CaCl_2$ (Williams and Steinbergs, 1959) or 0.1 M LiCl (Roberts and Koehler, 1968), and an adsorbed fraction extractable by $Ca(H_2PO_4)_2$ (Fox et al., 1964a), KH_2PO_4 (Ensminger, 1954), or $Ca(OH)_2$ (Williams and Steinbergs, 1962).

Typical values obtained for water soluble sulfate-sulfur in surface soils of humid regions are usually less than 10 ppm, which in many cases amounts to less than 5 percent of the total sulfur present. Some examples are given in Table 1.

According to Reisenauer (1967), most soils have the capacity to adsorb some sulfate, although the amount retained by soils at pH 6.0 and above is not significant. Normally, appreciable levels are associated with such soil characteristics as strong weathering, moderate to strong acidity, significant amounts of hydrous oxides of iron and aluminum, and kaolinitic clay minerals. Soils with these characteristics tend to contain considerably more adsorbed sulfate in

Table 1. Water soluble sulfur in soils

Source	Region	No. of soils	Water soluble S (ppm) Mean	Range	Extractant
Roberts and Koehler (1968)	Wash.	11	.91	(.34-2.65)	1 M LiCl
		11	1.00	(.52-2.47)	5 mM $MgCl_2$
Fox et al. (1964a)	Nebr.	24	7	(1.8-21)	water
Spenser and Freney (1960)	Aust.	24	10	(3-40)	water
Williams and Steinbergs (1962)	Aust.	28	9	(0.4-58)	.15% $CaCl_2$

their subsoils than they do in their surface layers. This is partly the result of saturation of the adsorption sites of the surface layer with other anions, especially phosphate, and to the higher clay content of the subsoil (Reisenauer, 1967).

The ability of soils to adsorb sulfate has much significance in the sulfur nutrition of crops; it is an important source of available sulfur for plants (Sanford and Lancaster, 1962; Barrow, 1967), and it retards the rate of sulfate movement in the soil, thereby reducing leaching losses.

The nature of sulfate adsorption sites in soils is not well understood. The studies made by Chao et al. (1962a), Chao et al. (1965), however, have resulted in the proposal of several possible mechanisms to explain the retention of inorganic sulfate by soils. Such mechanisms involve:

1. Anion exchange due to positive charges on hydrous iron and aluminum oxides or on the crystal edges of 1:1 clays at low pH values.
2. Retention of sulfate ions by hydroxy-aluminum complexes by coordination.
3. Salt adsorption whereby both cation and anion of the salt are attracted to the surface of the soil colloid.

4. Amphoteric properties of soil organic matter resulting in positive charges under certain conditions.

An anion exchange mechanism proposed by Chang and Thomas (1963) helps to explain the increase in sulfate adsorption with a decrease in soil pH. This mechanism suggests that SO_4 ions exchange for OH ions associated with the hydrous oxide coatings on the surface of Al saturated clay particles, R_x (OH)y [clay]. After exchange the adsorbed sulfate appears as R_x [(OH)y-z (SO_4)z] [clay], and displaced OH ions react with H ions formed by hydrolysis of Al in the presence of salt.

While water-soluble sulfate is considered to be readily available to plants, adsorbed sulfate may be less available. In some instances a high degree of correlation between SO_4-S extracted with a phosphate solution, and S uptake by greenhouse plants, has suggested that adsorbed phosphate is readily available (Spenser and Freney, 1960; Fox et al., 1964a). Furthermore, Chao et al. (1962a) with four successive water extractions removed 71-80 percent of the adsorbed sulfur from two acid Oregon soils, which suggests that adsorbed S would be readily taken up by plants. Barrow (1967) demonstrated, that given a reasonably long growing period, plants grown in greenhouse pots would extract from soil almost all the adsorbed sulfate initially present. However, in a recent study he (Barrow, 1969)

found that inorganic sulfate was not equally available on all soils. On soils which could adsorb large amounts of sulfate, the sulfate present is taken up more slowly than on nonadsorbing soils. In making a prediction equation to describe plant uptake of sulfur, he obtained a closer relationship by including both the sulfate present in the soil and the relative ability of the soil to adsorb sulfate.

Factors Affecting the Amount of Available Sulfur in Soils

The amount of available sulfur present in a soil at any given time depends on:

1. Sulfate retention, which is the ability of the soil to retain sulfate in the adsorbed form against removal by leaching.
2. The rate of addition of inorganic sulfur to the soil from both internal and external sources viz., mineralization of organic matter, accessions from the atmosphere, additions from fertilizers, groundwater etc.
3. The rate of removal of inorganic sulfate from the soil by plant uptake, by leaching, and possibly by gaseous losses under reducing conditions.
4. The rate of immobilization of inorganic sulfate by microorganisms.

Many aspects concerning additions to and removal from soil

of available sulfur have been discussed in reviews by Walker (1957), Jordan and Ensminger (1958), Freney et al. (1962) and Whitehead (1964).

In this review, factors affecting the level of available sulfur in soil will be discussed in terms of 1) soil factors and processes and 2) external factors operating on the soil.

Soil factors

Sulfate adsorption Sulfate adsorption is a measure of the soil's ability to retain sulfate-sulfur against leaching. Williams and Steinbergs (1962) estimated this characteristic by shaking their soils with a K_2SO_4 solution containing 12.5 ppm S at a ratio of 1:5 and measuring the S remaining in solution. Equilibrium studies of sulfate retention in soils have indicated that factors such as nature of the clay, presence of Al and Fe hydrous oxides, equilibrium pH, concentration of sulfate in the equilibrium solution, and the presence of other anions have marked effects on the amounts of sulfate adsorbed.

Soils containing clays predominantly of the kaolinitic type have the capacity to retain more sulfate than do those with clays mainly of the montmorillontic type (Chao et al., 1962b; Kamprath et al., 1956). Chao et al. (1962b) found that clays saturated with H^+ retained sulfate in the order kaolinite > illite > bentonite. However, when these clays

were saturated with aluminum, sulfate retention was similar for kaolinite and illite but lower for bentonite.

The greater retention of sulfate by kaolinite compared with montmorillonite has been attributed to a higher proportion of anion-exchange sites on 1:1 type clays, and a higher negative charge with associated anion repulsion on 2:1 type clays. Harward and Reisenauer (1966) have suggested that because hydrous oxides of Fe and Al are normally associated with kaolin minerals, sulfate adsorption attributed to the presence of 1:1 clays may, in fact, be influenced more by hydrous oxide contaminants than by the clay minerals themselves.

The amount of clay in soil also, appears to be of significance in retention of the sulfate ion. Increasing levels of adsorbed sulfate and of sulfate retention with soil depth are to a large extent dependent on the increasing clay content of the subsoil (Ensminger, 1954; Blakemore et al., 1968).

Studies by Hogg (1966) and Hogg and Toxopeus (1966) on volcanic ash soils in New Zealand, showed that SO_4 ions were readily leached from superphosphate applied to pumice soils containing less than 10 percent clay. Losses from yellow-brown loams, (soils more weathered than pumice soils) containing much allophanic clay, were extremely small, indicating the effect of the clay on SO_4 retention.

Hydrous oxides of iron and aluminum, which are important constituents of acid Latasols, Andosols (Chao et al., 1964) and Red-Yellow Podzolic soils (Kamprath, 1968), have been shown to be an important factor associated with sulfate retention (Ensminger, 1954; Chao et al., 1962b, 1964; and Kamprath et al., 1956). Evidence that Fe and Al oxides are directly associated with sulfate retention has been provided by Chao et al. (1962b). They removed Fe and Al oxides by chemical treatment, and the resultant soil showed a much lower sulfate retention. Furthermore, Chao et al. (1964) by coating recent alluvial soils of low sulfate retention, with hydrous Fe and Al oxides were able to increase the sulfate retention to levels comparable to those of highly retentive Ando soils. In the acid range, the amounts of SO_4 adsorption were found to be proportional to the amounts of Fe or Al oxides present. With increasing acidity, the Fe system showed increasing sulfate adsorption, whereas the Al system showed a maximum at pH 4.0. Aluminum oxides were found to be more effective in retaining sulfate than iron oxides, when both were present as surface coatings on soil particles. The work of this Oregon group (Chao et al., 1964) also suggests that where an appreciable amount of Al or Fe oxides are present (3-6 percent), under acid conditions, clay mineral type may cease to be a dominant factor in determining the capacity of the soils to adsorb

sulfate. This is thought to be due to masking of the adsorption sites on the clays by a continuous film of Fe or Al oxides on the soil particle surfaces.

Most studies indicate that sulfate retention is strongly dependent on equilibrium pH (Ensminger, 1954; Kamprath et al., 1956; Chao et al., 1962b and 1964); sulfate retention increases as the pH of the soil suspension is decreased. The effect of pH on sulfate retention was shown in the previous section to be dependent on the presence of hydrous oxides of Fe and Al (Chao et al., 1964). Earlier work by Kamprath et al. (1956) showed that the amount of sulfate adsorbed, increased with both the equilibrium concentration of sulfate in the soil solution and decrease in pH.

The presence of other anions will effect the retention of sulfate. Chang and Thomas (1963) have demonstrated that sulfate is weakly held relative to other common anions with strength of retention being of the order phosphate > sulfate > nitrate = chloride. Chao (1964) investigated the affect of 26 anions and found that all except 6, reduced sulfate adsorption to varying degrees. The most effective anions in reducing sulfate adsorption were phosphate, molybdate and fluoride among the inorganic anions, and oxalate, tartrate and gluconate among the organic anions. OH and HCO_3 ions decreased SO_4 adsorption by increasing the equilibrium pH of the soil suspensions. Anion effects

were explained by

a) competition for anion exchange sites,

b) ability of anions to form chelate complexes with Fe and Al, and/or

c) precipitation reactions.

The selection by Ensminger (1954) of the phosphate anion as an extractant of adsorbed sulfate, would therefore appear to be soundly based.

The effect on sulfate retention of adding phosphate and hydroxyl ions to soils has important practical implications. Ensminger (1954) reported that both superphosphate and lime applications decreased the capacity of soil to adsorb sulfate from calcium sulfate solutions. Similar results were obtained by Kamprath et al. (1956) who showed that sulfate adsorption was stopped on all soils when the $H_2PO_4^-$:SO_4^{2-} ratio reached 2/3 in terms of equivalent amounts. Liming will increase the soil pH, thereby decreasing the positive charge on the hydrous oxides of iron and aluminum, and, by increasing the activity of OH ions tends to displace adsorbed sulfate. The effect of liming is therefore to reduce the amount of sulfate adsorbed by soils.

Ordinary superphosphate (0-20-0) is often used to supply the phosphate and sulfate needs of a crop simultaneously. Because phosphate will be adsorbed preferentially and more strongly than will sulfate ions, there will be a tendency

for the sulfate not utilized by a growing crop to be leached to lower depths in the soil. On sulfur deficient soils in New Zealand, Lobb (1962) found that repeated annual applications of 2 cwt of superphosphate per acre failed to build up sufficient residual sulfate to provide the sulfur needs of pasture for a single season after the applications were discontinued. A similar problem has been encountered in West Australian soils (Barrow, 1967) where sulfur deficiency may reappear in the same year of application of superphosphate. The problem of sulfate leaching on soils deficient in both P and S, may be overcome by superphosphate fortified with elemental sulfur. This reduces leaching losses and provides a uniform supply of available sulfate throughout the year (Martin and Walker, 1966; Ludecke, 1965).

Mineralization and immobilization Where atmospheric sources of sulfur are low and no fertilizer sulfur or manure is added, plant growth will be dependent on sulfate-sulfur which has been released by mineralization of organic sulfur.

The mechanisms of mineralization of sulfur in soils are still largely unknown. A close relationship is known to exist between the amounts of carbon, nitrogen and sulfur in soil organic matter (Donald and Williams, 1954; Walker and Adams 1958; Whitehead, 1964). An average ratio of these elements in soil organic matter has been calculated to be 125:10:1.2. It has been suggested (Freney and

Stevenson, 1966; Williams, 1967a), that the processes of mineralization and immobilization of sulfur may be similar to those that exist for nitrogen. With cropping and cultivation, organic sulfur and total N decrease, but in general little change occurs in the N:S ratio (Jensen, 1963; Williams and Lipsette, 1966). This implies that in the long term, nitrogen and sulfur are mineralized in proportions similar to those occurring in organic matter. In the short term, data obtained by Nelson (1964) would support this hypothesis, but others, White (1959), Barrow (1961) and Williams (1967), have found that a greater proportion of mineral N to sulfate S, is released by mineralization. For example, Williams (1967b) in a group of Australian soils with an N: organic S ratio of 7.5:1, found over a 12-week period, the ratio of nitrogen to sulfur mineralized ranged from 10.2 to 45 with a mean of 19.0. There was no relationship between the amount of N and S mineralized and the nitrogen or organic S content of soil. However, Nelson (1964) found that there was a direct relationship between sulfate released from soil during incubation under moist conditions and the S content of the soil ($r = 0.93$). No such relationship however was found to exist for Oregon soils (Harward et al., 1962).

Barrow (1960) found that the C:S ratio provided a rough guide to the ability of a soil to release S on

incubation. For example, if the C:S ratio was less than 200, sulfate would accumulate, if the ratio was above 400, sulfate was immobilized, whereas, if the ratio was between 200 and 400, sulfate could be either released from or tied up in the organic matter.

Soil sulfate, like nitrate, is subject to immobilization through microbial activity. Barrow (1958) has shown, that in the presence of easily decomposed low-sulfur organic materials, soil organisms may compete with higher plants for the inorganic sulfate available. In greenhouse experiments it has been demonstrated, that the addition of starch (Conrad, 1950) or the incorporation of highly carbonaceous plant residues (Nearpass and Clark, 1960; Stewart and Whitfield, 1965) reduced the availability of soil sulfate. A yield depression of N fertilization, which was reversed by adding sulfur to a field experiment with wheat in Washington, was attributed to sulfate immobilization (Reisenauer and Leggett, 1957).

Conditions which affect mineralization of soil sulfur are not well understood, but they are believed to be similar to those affecting N mineralization (Williams, 1967a). Thus Williams (1967b), found that no mineralization of sulfur occurred at 10° C or below, but the rate of release increased with temperature up to 30° C. The effect of soil moisture was very similar for both release of sulfate and

nitrate (Williams, 1967b) with mineralization being markedly reduced by adjusting the moisture content of the soil to values appreciably above or below field capacity.

Incubation with calcium carbonate has been found to increase the release of extractable sulfur (White, 1959; Nelson, 1964 and Williams, 1967b). Possible mechanisms of release will tend to vary with the nature of the soil incubated, viz.,

a) With a more favorable pH in acid soils, bacteria will release sulfur more readily from organic matter (Freney and Stevenson, 1966).

b) Release of sulfate from organic matter by chemical hydrolysis at pH values above 7.0 (Barrow, 1960).

c) Release of adsorbed sulfate from exchange sites by OH ions, and by reduction of sulfate adsorption capacity (Williams and Steinbergs, 1962).

d) Release of sulfate added in calcium carbonate to acid soils (Williams and Steinbergs, 1962; 1964).

Mineralization of sulfur was suppressed by the addition of formaldehyde or toluene (Williams, 1967b).

Drying of soils generally results in an increase of extractable sulfate (Williams, 1967a). However, Williams (1967b) found that many soils, after air-drying and storage, contained less $CaCl_2$-extractable S than those incubated without prior drying. Incubation after drying and rewetting,

gave a rapid flush of S mineralized during the first few days of incubation, after which mineralization was similar to that of the original undried soil (Williams, 1967b). Some soils, collected after they had been in a dry state in the field for several months, did not show this type of mineralization even though they had done so when collected moist and had been air-dried in the laboratory. On the other hand, Barrow (1967) working with West Australia soils found there was more S mineralized during incubation from soils sampled in early fall after a long dry summer than those sampled in the spring.

The presence of growing plants in soils is believed to stimulate mineralization of organic sulfur (Freney and Spenser, 1960). In a greenhouse experiment Spenser and Freney (1960) found that mobilization of organic S occurred where up to 36 ppm SO_4-S was added to soils planted to Phalaris tuberosa. In the absence of plants there was no net mineralization of organic S after addition of sulfate. Increased mineralization is believed to be either the result of enzymic decomposition following the excretion of enzymes from plant roots (Freney and Stevenson, 1966) or due to the activity of rhizosphere microorganisms (Freney and Spenser, 1960). Such sulfatases have been recognized and assayed in soils (Tabatabai and Bremner, 1970a; 1970b) in particular, aryl sulfatase will hydrolyse organic sulfate

esters to inorganic sulfate and organic hydroxyl compounds.

External factors

Climate Precipitation and temperature are very important components of the climate influencing the level of available sulfur in the soil through mineralization and leaching of S. Wherever rainfall is in excess of evapotranspiration, downward movement of water in the soil will occur causing some leaching of sulfate. On coarse-textured soils with near neutral reaction, leaching losses of sulfur can be considerable during periods of heavy rainfall (Reisenauer, 1967). For example, McKelly and Williams (1960) found that 78 percent of the sulfur applied at the rate of 100 lb. and 300 lb. per acre of gypsum was leached from a sandy loam in the growing season following fertilization. The ability of soils to adsorb sulfur, as discussed earlier in this review, will bring about a considerable reduction in such leaching losses.

Where evapotranspiration greatly exceeds rainfall, sulfates tend to accumulate in the soil. Such accumulations may occur in the subsoil; or, where drainage is poor, sulfates will even accumulate in the surface horizon. Soils of the semi-arid and arid regions of the United States should, therefore, contain adequate sulfate for crop needs.

Temperature influences the supply of available sulfur in soils through its affect on mineralization and leaching.

In cool temperate regions, low temperatures during winter, by freezing of the upper soil horizons, reduce leaching losses of sulfate, Furthermore, in early spring the amount of inorganic sulfate in the surface horizon may be limiting for crops or pastures because soil temperatures are too low for mineralization of organic sulfate.

Therefore, on the basis of rainfall and temperature, greater losses of sulfate by leaching would be expected under warm temperate and tropical conditions than under cool temperate or arid climates.

Atmospheric supply Several gaseous forms of sulfur are found in the atmosphere--SO_2, H_2S and CH_3SH. These sulfur compounds may be carried down with precipitation and deposited in the soil or they may be absorbed directly from the air by soils and plants. Whitehead (1964, p. 4) states "that the amount of available sulfur in the soil is of prime importance for plant nutrition in some areas of the world, whereas in other areas, the quantity supplied by the atmosphere or by fertilizer application, makes the native soil supply relatively insignificant."

In humid regions away from industry and urbanization, the occurrence of sulfur deficiency in crops is in part a consequence of a low atmospheric supply of sulfur. Such is the case in Eastern Australia, New Zealand and the Northwest and Southeastern regions of the United States. White-

head (1964) has summarized published data on the amount of sulfur brought down in rainfall, and shows that this can range from less than 1 lb. per acre per year in some inland areas of Australia, New Zealand and Africa to more than 120 lb. S per acre per year in the vicinity of industrial cities. In coastal areas 2-4 lb. per acre of the deposited sulfur is derived from the ocean, but the bulk of it is derived from the combustion of coal and other fuels (Freney et al., 1962).

Besides the sulfur brought down in precipitation, it has been established (Bertramson et al., 1950) that an amount similar to that in precipitation, in the form of sulfur dioxide and possibly other gases, is absorbed directly by both soils and plants. Using a water culture technique and radio-sulfur tracers Olsen (1957) demonstrated that cotton, supplied with adequate sulfate in solution, would obtain about 30 percent of its sulfur from an atmosphere which contained 0.01 to 0.05 ppm SO_2. Sulfur deficient plants obtained up to 90 percent of their sulfur from the atmosphere. Similarly Jensen (1963) using a variety of plants showed that they obtained 22 to 36 percent of their sulfur supply by direct absorption from the atmosphere.

A study made at varying distances from an oil-burning plant in Sweden (Johansson, 1959), indicated that sulfur added directly from the air, exceeded by a factor of three

or more, that added through precipitation. Thus, it seems likely that estimates of atmospheric contributions of sulfur to soil based on the sulfur content of the rainfall, may grossly underestimate this source of sulfur supply to the soil.

Fertilizers, manure and irrigation water In many areas where the atmospheric supply of sulfur is low and mineralization of organic S is not sufficient for the needs of crops or pastures, the available sulfur supply in the soil has been maintained at a favorable level, incidentally, by regular application of ordinary superphosphate (which contains appreciable amounts of sulfur), to correct phosphate deficiency (Walker, 1957). In parts of Europe, sulfur needs will also have been met where ammonium sulfate has been used as a source of nitrogen. The sulfur content of a wide range of fertilizer materials has been compiled by Tisdale and Nelson (1966).

The regular application of animal manures to soils will also help maintain a favorable level of available sulfate for crop growth. Benne et al. (1961) reports that the sulfur content of various animal manures ranges from 1-6 lb. S per ton which is of the same order as that reported for phosphorus. Thus, an application of 10 tons per acre of farmyard manure would fully provide the sulfur requirements for most crops.

Irrigation water can contribute sufficient sulfur for the needs of a growing crop. In Nebraska, sulfur in the ground-water ranges from 3-4 lb. to more than 1500 lb. per acrefoot. An average figure for the state is about 45 lb. per acrefoot (Fox et al., 1964b). Thorne and Peterson (1954) quote similar values for 19 rivers used for irrigation purposes in the Western United States. Sulfur contents ranged from 3 to 1850 lb. S per acrefoot with the majority being greater than 40 lb. S per acrefoot.

Cropping system The depletion of available sulfur in soil depends on the crop grown, its yield, and the proportion of the crop removed from the field at harvest. Some crops require greater amounts of sulfur than others. The sulfur requirements of a number of economic crops has been tabulated by Coleman (1966) who points out that grasses and cereal crops require lesser amounts of sulfur (8-12 lb. S/acre) than do legume and cruciferous crops (20-35 lb. S/acre). The ability of a crop plant to send its roots deeply into the subsoil will often enable it to obtain a more plentiful supply of sulfur than will a shallow-rooted plant. For example, alfalfa may obtain an abundant supply of sulfur from subsoil sources, compared to shallow-rooted grasses and clovers which, on the same soil, could be sulfur deficient because of a low level of available sulfur in the surface soil (Blackmore et al., 1969).

Methods of Determining Available Sulfur in Soils

Chemical methods

Inorganic sulfate in soils of humid regions is known to be readily available to plants (Barrow, 1967), but in many soils only a few parts per million can be extracted at any given time. However inorganic sulfate is being continually replenished by atmospheric sulfur and by mineralization from organic sources in the soil. Therefore, chemical methods which are designed to provide a reliable index of the available sulfur status of soil should estimate not only the inorganic sulfur immediately available to plants, but also that fraction of the organic sulfur which will be mineralized in the presence of plants. A comprehensive survey of existing methods for the determination of sulfate and extractable sulfur in soil has been prepared recently by Beaton et al. (1968).

While the nature of available S in soil is not well understood, it is generally conceded (Ensminger and Freney, 1966) that water soluble sulfate, adsorbed sulfate and a labile fraction of soil organic S constitute the three principal fractions. The wide array of extractants that have been used to extract available S (Reisenauer, 1967; Beaton et al., 1968) will extract one or more of these fractions of available sulfur. In the following section some of the more popular methods in use will be discussed, according

to the fraction(s) of available S extracted.

The water-soluble fraction, which in some soils is the major component of inorganic S (Fox et al., 1964a), has been extracted by cold water (Freney, 1958; Spenser and Freney, 1960; Nelson, 1964) or neutral salt solutions such as 0.15 percent calcium chloride (Williams and Steinbergs, 1959), 0.1 M lithium chloride (Arkley, 1961) and sodium chloride (Williams and Steinbergs, 1959). Sodium acetate (Ensminger, 1954) also extracts essentially water soluble S. Although water is the simplest extractant for sulfate sulfur it tends to deflocculate the soil making filtering difficult, and, in addition, it may extract some organic sulfur not readily available to plants. The use of calcium or sodium chloride maintains the soil in a flocculated condition thereby producing clear extracts, which contain practically no organic S (Spenser and Freney, 1960).

Soluble sulfate plus adsorbed sulfur is extracted by phosphate solutions (Ensminger, 1954; Fox et al., 1964a), calcium carbonate suspensions (Williams and Steinbergs, 1962), and neutral N ammonium acetate (McClung et al., 1959). A solution of KH_2PO_4 containing 500 ppm P has been widely used to estimate the sulfate S status of soils. Fox et al. (1964a) found $Ca(H_2PO_4)_2$ preferable to KH_2PO_4 because while it gave values similar to KH_2PO_4, it also produced extracts essentially free of colloidal material, which is

often a problem with KH_2PO_4. The use of phosphate solutions may give low values on soils containing gypsum; the gypsum particles become coated with calcium phosphate thereby inhibiting their solution (Spenser and Freney, 1960).

Methods which are designed to extract a labile fraction of the soil organic S, in addition to water soluble and adsorbed S, include heat soluble S and hot water soluble S (Williams and Steinbergs, 1959; Spenser and Freney, 1960; and Fox et al., 1964a) and 0.5 M $NaHCO_3$, pH 8.5 (Kilmer and Nearpass, 1960). The sulfur obtained using these extractants has been found to range from two to four times that extracted using phosphate solutions (Fox et al., 1964a). The $NaHCO_3$ extractant produces extracts that are highly coloured by solvated organic matter. According to Reisenauer (1967), sulfate determination by direct reduction will measure a fraction of this organically combined S, presumably organic sulfates. Treatment of colored extracts to eliminate organic matter interference for turbidimetric sulfate determination, by either nitric and perchloric acid digestion (Fox et al., 1964a), or with hydrogen peroxide (Williams and Steinbergs, 1959) will give higher values for extractable S. Addition of carbon to the sodium bicarbonate system will reduce the amount of S extracted to approximately the amount obtained with a KH_2PO_4 solution (Reisenauer, 1967).

Following extraction, sulfate-sulfur is most frequently determined on a portion of the extract, using either the colorimeter methylene blue procedure (Johnson and Nishita, 1952) or the barium sulfate turbidimetric method (Chesnin and Yien, 1950).

Williams and Steinbergs (1959) compared dry heating at 100° C to heating with water to dryness on a steambath prior to extraction with 1.0 percent NaCl. Maximum amounts of sulfur were extracted where soils had been heated moist, and this fraction was referred to as heat-soluble S. It was found to be highly correlated with total water soluble, $CaCl_2$ extractable, and sulfur extracted by oats grown in pot culture. In general, heat soluble S was from two to three times higher than $CaCl_2$-extractable S.

Biological methods

Biological methods that have been used to measure S availability include "A" and "a" values, bioassay with algae and Aspergillus, incubation, and Neubauer techniques.

"A" values measured by the technique of Fried and Dean (1952) for phosphorus, have been used for sulfur. Kilmer and Nearpass (1960) found that "A" values were correlated with bicarbonate-extractable S. In Oregon soils, Harward et al. (1962) found that "A" values provided a useful index of sulfur availability. Sulfur "A" values were highly correlated with percent sulfur in alfalfa and with extract-

able plus "sulfate release" for the soils.

Closely related to "A" values, "a" values provide an index of sulfur availability especially useful for assessing the relative nutrient status of soils that do not respond to the nutrient applied. This method, originally proposed by Steenbjerg (1951), extrapolates the yield of nutrient curve to the X axis. McClung et al. (1959) in a greenhouse experiment with Brazilian soils obtained "a" values that were closely related to responses to applied sulfur.

Bioassay with algae and Aspergillus has been found to correlate with dry matter yields and sulfur uptake by greenhouse plants, equally as well as the better chemical methods (Spenser and Freney, 1960; Naik and Das, 1964; Cullimore, 1966). Using Aspergillus niger, Spenser and Freney (1960) found that the fungus extracted a quantity of sulfur similar to that extracted by phosphate, which suggests that Aspergillus is able to utilize both free and adsorbed sulfate.

Incubation procedures designed to measure the capacity of a soil to convert organic S to inorganic sulfate should, at least on theoretical grounds, provide an index of the sulfur status of a soil in the same way as has been used for nitrogen. So far, incubation studies have not been successful in providing an index of the available S status

of soils, since only small quantities of sulfur have been released (White, 1959; Barrow, 1961, Harward et al., 1962).

Greenhouse tests of various types have been used to measure the amount of sulfur available to plants. These greenhouse estimates of the sulfur supplying ability of the soils are frequently used as a basis for evaluating chemical methods of estimating available sulfur. Greenhouse tests range from Neubauer-type extractions whereby a large number of plants are grown on a small amount of soil for a short period of time (17 days), to long term experiments of several months, using fewer plants and a larger quantity of soil. In short term experiments such as those reported by Cairns and Richer (1960), Sanford and Lancaster (1962) and Rehm and Caldwell (1968), the test plants barley, turnips and grain sorghum respectively, were grown in a small quantity of soil so that the roots within a short time interval, would thoroughly penetrate the soil and exhaust the available sulfur supply. In long term experiments, such as those reported by Spenser and Freney (1960), Fox et al. (1964a) and Barrow (1967), test plants such as Phalaris tuberosa, alfalfa and ryegrass which can be harvested periodically, were grown in 1 kg or more of soil. In these experiments the supply of available sulfur was frequently exhausted by the test plant and an estimate of the rate of mineralization of organic sulfur was made, by deducting from plant uptake

of sulfur, the decrease in adsorbed plus water soluble S components of sulfate sulfur in the soil (Spenser and Freney, 1960).

Evaluation of Laboratory Methods for Estimating Available Sulfur in Soils

Laboratory methods for determining available sulfur in soil are normally evaluated by correlation of results with response from and uptake of sulfur by greenhouse plants. High correlation coefficients are obtained where S uptake by the plant, and S extracted chemically, both remove the same component of soil sulfur. For example, Fox et al. (1964a) on Nebraskan soils obtained correlation coefficients of 0.952 and 0.936 by relating sulfur uptake by alfalfa over 4 cuttings, to the sulfur extractable by calcium phosphate and water, respectively. Chemical methods which extracted sulfur associated with organic matter i.e., heat-soluble S and autoclave-soluble S gave lower correlations with S uptake. Spenser and Freney (1960) obtained high correlations between S uptake by Phalaris tuberosa and cold-water-extractable sulfur, hot-water-extractable sulfur and Aspergillus sulfur. The correlation coefficients were 0.926, 0.920 and 0.912 respectively. When three nonresponsive (high available S) soils were omitted from the data, the strongest correlations were then obtained between Aspergillus S and phosphate extractable S. These workers stress the considerable influ-

ence that a few high values can have on the correlation. Using a group of mainly acid, East Australian soils, Williams and Steinbergs (1959) studied the relationship between sulfur uptake by oats grown to flowering in a greenhouse and sulfur extracted in the laboratory. The best correlation with S uptake by oats was that obtained by extracting S with water at 100° C after the soil had been heated for one hour at 102° C ($r = 0.90$). Correlations with total water soluble and 0.15% $CaCl_2$ extractable sulfur gave correlation coefficients of 0.80 and 0.78 respectively. Thus, it would appear that with certain groups of soils differences in S uptake between soils are perhaps more dependent on the labile fraction of organic sulfur than on the readily extractable water soluble and adsorbed sulfur.

Bardsley and Lancaster (1960) also found the organic sulfur fraction important in determining the available sulfur supply in surface soils. Reserve sulfur, which is organic S plus reduced inorganic S, was found to be highly correlated with yield of sulfur from three harvests of white clover ($r = 0.790$). Sulfate sulfur, extractable with ammonium acetate was not significantly related to sulfur yield.

Kilmer and Nearpass (1960) considered that any estimate of available sulfur should include that portion of the organic sulfur which would be mineralized during the growing

season. They found that 0.5 M $NaHCO_3$ at pH 8.5 correlated best with "A" values ($r = 0.89$). Both extractable S and "A" values showed a similar relationship to yield response. Soils containing less than 10 ppm of $NaHCO_3$-extractable S were responsive to sulfate applications in a greenhouse test with cotton.

The readily available sulfate status of 40 Mississippi soils was estimated by Sanford and Lancaster (1962) using biological and chemical methods. A modification of the Stanford and DeMent (1957) method, using turnips pregrown in silica sand, was employed to extract available sulfur over an 8-day period. During this period, 68 percent of sulfate S extractable by ammonium acetate (0.5 N) plus acetic acid (0.25 N), was absorbed by plants from surface soils, and 59 percent from subsoils. The correlation coefficient between S uptake by plants and sulfate S, chemically extracted, was 0.87.

Similarly, Roberts and Koehler (1968) used a short-term Stanford and DeMent (1957) technique to evaluate two chemical methods for extracting available sulfur from eastern Washington soils. Wheat plants were pregrown in sand culture and then "nested" in 200 g of soil for three weeks. Sulfur uptake in wheat plants was correlated with sulfur extracted by 0.1 M LiCl and 5 mM $MgCl_2$ from 53 surface and sub-surface soil samples. Correlation coeffi-

cients were 0.89 and 0.86 respectively. In general, the sulfur extractable in either LiCl or $MgCl_2$ was low in surface soils, averaging less than 1 ppm S. In half of the soils extractable S increased with depth while in the remainder it was relatively constant.

A Neubauer type of greenhouse procedure was employed by Rehm and Caldwell (1968) to assess the S supplying capacity of 79 Minnesota soils. The sulfur uptake by grain sorghum grown for 21 days, was highly correlated with sulfur extracted with calcium phosphate, sodium bicarbonate and ammonium acetate on coarse-textured gray-brown podzolic and gray wooded soils of the north central region of the state. Soils from the southern and western regions were found to be high in extractable sulfur and significant correlations were not obtained between S uptake by plants and extractable sulfur. Over all soils, there were no significant relationships between S uptake by sorghum and soil S extracted by calcium phosphate, sodium bicarbonate or ammonium acetate ($r = 0.117$, 0.132 and 0.029).

The nature of the S uptake data given in their paper, suggests a possible explanation for the lack of correlation between plant and soil data. Where soils contain adequate to high levels of extractable sulfur, differences in dry matter yield between soils will be small where nutrients other than S are kept at an optimum level. Even where data

from soils of low-S supplying capacity was included, only a narrow range of dry matter was obtained (0.71 to 1.09 g). Moreover, the range of sulfur concentration in the dry matter (0.216 to 0.295% S) was, in part, a consequence of a very short growing period. Over 21 days, the sorghum seedlings would derive a considerable part of their sulfur from the seed. Calculations suggest that, assuming 1g of seed (40 seeds) containing 0.15% S was used, up to 1.5 mg S was available to the plants. The range of sulfur yield in sorghum tops was 1.6 to 3.4 mg S. It is probable that more meaningful relationships would have been obtained had the growth period been extended to the point where the available sulfur was exhausted in the soils that had low sulfur-supplying power.

While greenhouse experiments are generally used to evaluate laboratory methods of assessing the availability of extractable sulfur, Bardsley and Kilmer (1963) have attempted to relate the amount of chemically extractable sulfur in soils of the southeastern United States, to the percent yield of field-grown crops. Percentage yield is defined as the yield of no-sulfur plots as a percentage of the mean yield of sulfur-treated plots. The best correlations were obtained for acetate-soluble sulfate and bicarbonate-extractable sulfur in the surface foot of soil ($r = 0.55$ and 0.59). Relationships between laboratory data

and field yield data cannot be expected to be as high as those obtained from greenhouse studies. While laboratory procedures can be carried out under rigidly controlled conditions, crop yields in the field are influenced by many factors other than the nutrient being studied.

In Nebraska, Fox et al. (1964a) obtained good correlation between both water and calcium phosphate-extractable sulfate and sulfur uptake by alfalfa under greenhouse conditions. The calcium phosphate-extractable sulfur in soils was then related to the field response of alfalfa and corn, to applied sulfur. On the basis of a limited number of soils, they predicted that responses to applied sulfur are assured on field crops of alfalfa and corn where the phosphate-extractable sulfur is less than 6 and 4 ppm, respectively. This calibration appeared to be reliable where subsoils were sandy in texture, but was unpredictable where textures were finer.

EXPERIMENTAL MATERIALS AND METHODS

Soils

Selection of sites

One of the primary objects of this study was to determine a suitable index of sulfur availability for Iowa soils. An essential requirement for this type of work is the selection of a number of soils which will exhibit a wide range in available sulfur supply.

In other areas it has been found that the amount of available sulfur present in soil can be related to such properties as amount and type of clay (Chao et al., 1962b), soil reaction (Kamprath et al., 1956), and organic matter content (Spenser and Freney, 1960). By selecting a number of soils showing considerable variation in the above correlative properties, it was expected that soils with a wide range of sulfur supplying power would be obtained. The analyses of Brown and Kellogg (1915) and Erdman and Bollen (1925) were of limited value in this respect.

Some characteristics of the soil sites and their location are shown in Table 2 and in Figure 1. A range in texture and organic matter content was obtained by taking a sequence of loess soils from southwest Iowa which have been shown (Ruhe, 1969) to decrease in particle size with increasing distance from the source of the loess. Moreover, because rainfall increases somewhat from west to

Table 2. Soil types, locations and crop rotations on sites from where the samples were collected and the experiments in which each soil was used

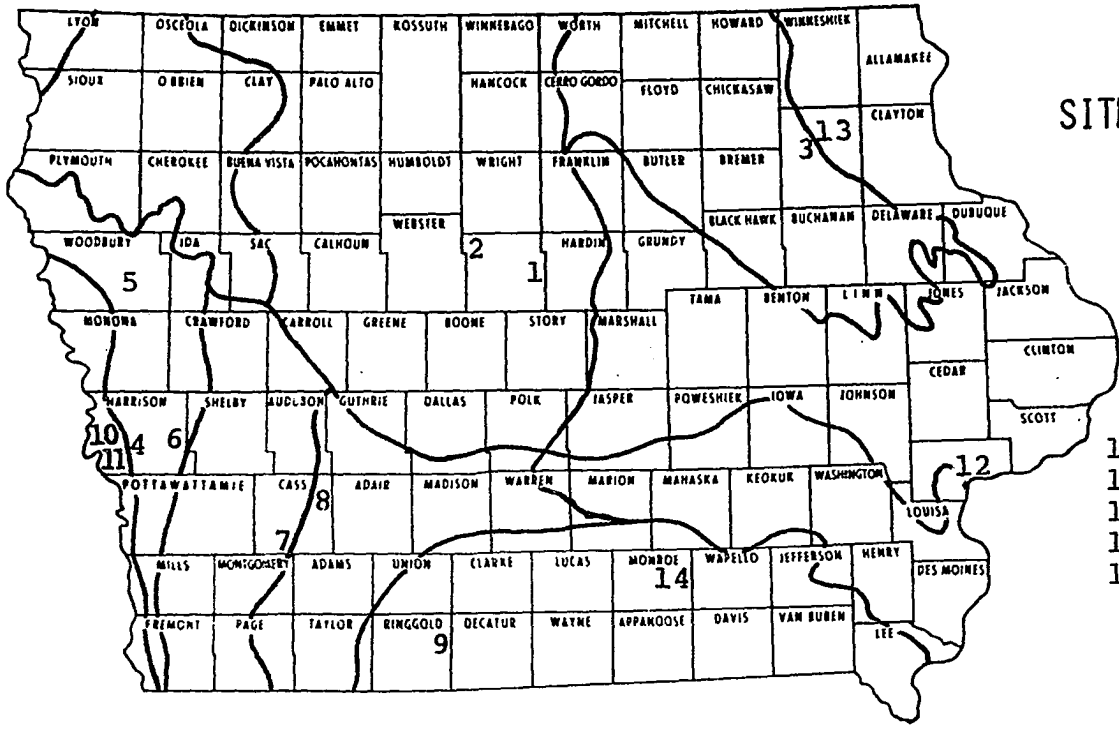
Lab no.[a]	Soil type	County
1, 17	Clarion l	Hamilton
2, 18	Webster cl	Hamilton
3	Hagener ls	Fayette
4	Hamburg sil	Harrison
5	Ida sil	Woodbury
6, 19	Monona sil	Harrison
7	Marshall sicl	Cass
8	Sharpsburg sicl	Cass
9	Grundy sicl	Ringgold
10	Albaton sicl	Harrison
11	Sarpy l	Harrison
12	Tama sil	Muscatine
13, 20	Fayette sil	Fayette
14, 21	Weller sil	Monroe
15	Thurman s	Dixon, Nebr.
16	Dorset sl	Hubbard, Minn.

[a]Both surface and subsoil (18-24 in) samples collected from Clarion, Webster, Monona, Fayette and Weller sites.

[b]C = corn, F = fallow, G = native grassland, M = legume meadow, O = oats, Sb = soybeans, crop in 1968 underlined.

Corn yield study site no.	Crop rotation[b]	Soil used in experiments no.
38	SbMSbC	1, 2, 3
48	SbCSbC	1, 2, 3
17	SbCCF	1, 3
-	G	1, 2, 3
46	CMMM	1
37	CSbC	1
42	MCCC	1, 2
23	SbCOMC	1, 3
-	CCSb	1
29	CSbC	1
44	CMC	1, 2
9	CSbC	1, 2
8	CCCC	1, 3
-	SbCCC	1
-	-	1
-	-	1

Figure 1. Map of Iowa, showing location of sites from where soil samples were obtained, for Experiments 1/68, 2/68 and 3/69



SITE NO. SOIL SERIES

1	CLARION
2	WEBSTER
3	HAGENER
4	HAMBURG
5	IDA
6	MONONA
7	MARSHALL
8	SHARPSBURG
9	GRUNDY
10	ALBATON
11	SARPY
12	TAMA
13	FAYETTE
14	WELLER

east along this sequence of soils, both organic matter levels and leaching of calcium carbonate tend to increase with distance of the soil from the loess source.

Several coarse-textured soils were included, namely a loamy sand from Fayette County, a sand from northeastern Nebraska and a sandy loam from north central Minnesota. Both out-of-state soils have been classed as sulfur deficient (Fox et al., 1964b; Seim et al., 1969) and were included to provide soils of low sulfur-supplying capacity in correlation studies. Other soils used in this study include those formed on glacial till from north central Iowa, forest loess soils from eastern and southern Iowa and Missouri bottom land soils. Some subsoil samples (18-24 inch) were also collected from certain sites so that availability of sulfur in subsoils could be compared with that of corresponding surface soils. Many of the sites shown in Table 2 are those employed by L. C. Dumenil in his Corn Yield Study, Project No. 1377. On these sites the soil type has been verified and profile descriptions have been made by Soil Survey personnel of the U.S.D.A. Soil Conservation Service. Also, records of cropping history and fertilizer use have been kept, and data on corn yield, soil test levels and rainfall have been collected for the past eight years. In the selection of sites for this study care was taken to ensure that neither animal manure nor

sulfur-containing fertilizers, such as superphosphate, had recently been applied. In this way it was intended that the sulfur status of the soils to be evaluated would reflect that inherent to the soil itself, together with accessions received from the atmosphere, rather than the effects of recent management.

Collection of samples, preparation and storage

Experiment 1 Bulk soil samples of approximately 100 lb., from the 0-6 inch depth, and a limited number from the 18-24 inch depth, were collected during the latter part of July, 1968. Most of the samples were taken from between the rows in cornfields, care being taken to disturb the corn as little as possible. The soils were placed in plastic-lined burlap sacks and were stored until required, in a cool situation. During August each bulk sample in the field-moist state, was passed through a 1/4 inch mesh screen to remove nonsoil material and to reduce the soil aggregates to a degree of fineness usually considered to be suitable for greenhouse investigations.

Each bulk sample was then thoroughly mixed, sampled for moisture content, and a 10 lb. subsample was taken for chemical and physical analyses. A sample was also taken at this time for available nitrogen, phosphorus and potassium and pH analyses and, prior to analyses was stored with the 10 lb. sample at 3° C in a refrigerated room. The

remainder of the bulk sample was placed in double-layered polyethylene bags, sealed to maintain moisture content and stored in a cool place until potting.

Experiment 2 Experiment 2 was conducted to examine the effect of air-drying of the soil on the availability of sulfur to plants. The soils were selected to provide a range in organic matter and texture. For this study, additional bulk samples of about 100 lb., from the 0 to 6 inch depth of the original sites (Table 2), were collected in late November, 1968.

The methods of collection and screening were the same as those used in Experiment 1. After thoroughly mixing the screened soil, the bulk sample was divided into two 40 lb. portions. One part was stored undried in double polyethylene bags and the other was rapidly air dried at 35° C until no further loss of moisture could be detected. Subsamples for chemical analyses (5 lb.), and for available nitrogen, phosphorus and potassium and pH were taken from both dried and undried bulk samples.

Experiment 3 In order to study changes in available sulfur content with time and depth under field conditions, soil samples were taken from six sites (Table 2), at three times during the 1969 growing season. Samples to a depth of four feet were collected at corn planting, at silking and shortly after harvest. In May just after planting, a

sampling area 30 feet by 30 feet, divided into four plots each 15 feet by 15 feet, was marked out at each site. This sampling area was located adjacent to the corn yield site of L. C. Dumenil, and to the site from which the bulk soil samples for Experiments 1 and 2 were collected. At each sampling date, on each plot, one composite sample consisting of four cores was taken for each of five depths down the profile. The depth samples were from 0 to 6, 6 to 12, 12 to 24, 24 to 36 and 36 to 48 inches below the soil surface. The composite samples were then treated as follows: following brief storage at 3° C, subsamples were taken for moisture content. The sample was then rapidly air-dried and screened through a 2 mm mesh sieve and stored prior to analysis for available sulfate.

Laboratory Methods

Soil analyses

Field moist samples stored at 3° C were analyzed in the Iowa State University Soil Testing Laboratory for available nitrogen, phosphorus, potassium and pH. Ammonium-N present in the soil before and after anaerobic incubation at 40° C for 1 week, was determined by steam distillation of 5 g of soil in 10 ml of water, with 18 ml of 2.7 N KCl and 0.15 g of ignited heavy MgO. The distillate was trapped in 5 ml of boric acid-indicator solution and the NH_4 was titrated with 0.0179 N H_2SO_4. Ammonifiable N was obtained

by difference. Nitrate-N initially present, was determined by the addition of 0.4 g of finely ground DeVarda's alloy to the distillation flasks, after distillation of the initial ammonium, and redistilling and titrating the NH_4 collected in the boric acid solution.

Extractable phosphorus was determined by shaking the soil with Bray No. 1 extractant (0.025 N HCl and 0.03 N NH_4F), with a soil to extractant ratio of 1:10. To an aliquot of filtrate was added ammonium molybdate-HCl solution plus a reducing agent containing 1-amino-naphthol-4 sulfonic acid, sodium sulfite and sodium pyrosulfite. The blue color which developed was read after 15 minutes in a colorimeter using a red filter (660 mμ).

Exchangeable K was determined by extracting 2 g of soil with 10 ml of N ammonium acetate for 5 minutes, filtering and measuring the concentration in a flame photometer, using 100 ppm Li as an internal standard. Soil pH values were determined using a 1:2 soil:water ratio and a glass electrode pH meter.

Total carbon in soil was determined using a Leco automatic 70-second carbon analyzer. In this method (Tabatabai and Bremner, 1970a), a 0.2 to 0.4 g soil sample is treated with combustion accelerators (iron, tin and tin-coated copper) and heated to more than 1650° C in a stream of pure oxygen, in a high frequency induction furnace. The gases

evolved are passed through a series of traps to remove metallic oxide dust, sulfur oxides, nitrogen oxides, halogen gases, and water vapor and through a heated catalyst tube to convert CO to CO_2. The purified CO_2-O_2 mixture is analyzed for CO_2 in a thermistor-type thermal conductivity cell.

Total sulfur in soil was determined according to Tabatabai and Bremner (1970b), by wet oxidation of soil sulfur compounds to sulfate using alkaline sodium hypobromite solution. In this method a finely ground soil sample containing 10-50 mg of sulfur (about 0.1-0.2 g) is digested in a 50 ml digestion-distillation flask with 3 ml of sodium hypobromite solution on a sand-bath at 250-260° C. Heating of the flask is continued after taking to dryness and the residue is taken up in 1 ml of water. One ml of formic acid and 4 ml of reducing mixture (hydriodic acid, formic acid and hypophosphorus acid) are added and the flask is connected to a digestion-distillation unit. Sulfate in the digested sample is determined according to the procedure of Johnson and Nishita (1952).

HI reducible sulfur was determined according to Freney (1957) by digestion of 1 g of soil with a mixture of hydriodic, formic and hypophosphorus acid in a modified Johnson Nishita apparatus (Tabatabai and Bremner, 1970b). This fraction termed "HI reducible sulfur" is assumed by

Lowe (1964) to consist of organic sulfate and inorganic forms of sulfur. The reduced sulfur is finally determined colorimetrically by the methylene blue method.

"Carbon-bonded" sulfur was determined according to Lowe and DeLong (1963) by digestion of 0.1-0.5 g soil with 0.1 g of Raney nickel alloy, 5 ml of 5% NaOH and 25 ml of distilled water, in a 150 ml flask attached to the Johnson Nishita digestion-distillation unit. After 30 minutes heating, the flask is cooled, excess HCl (5 ml 1:1 HCl) is added and the digestion continued for a further 30 minutes. The H_2S evolved is trapped in a zinc acetate solution and the sulfur present is measured colorimetrically by the methylene blue method.

In order to estimate by chemical methods, inorganic sulfur that is readily available to plants, three different extractants were used. Each of these extractants have been found, under certain soil conditions, to extract amounts of sulfur that are highly correlated with plant uptake of sulfur. The extractants used were:

1. LiCl, 0.1 M solution as described by Arkley (1961).
2. $Ca(H_2PO_4)_2H_2O$, at 500 ppm P according to Fox et al. (1964b).
3. $NaHCO_3$, 0.5 M adjusted to pH 8.5 with NaOH according to Kilmer and Nearpass (1960).

Extractions of sulfate were made on both air-dried and

field moist samples at soil extractant ratios of 1:5 and 1:10. Ten grams of air-dried soil or its field moist equivalent were extracted by shaking for 30 minutes in a reciprocating shaker with 50 ml of extractant (1:5) in an 80 ml polypropylene centrifuge tube. Five grams of soil were used and 50 ml of extractant were used to obtain a 1:10 ratio. After shaking, the tubes were centrifuged at 2400 rpm for 15 minutes, a procedure which, in most cases, produced a clear supernatant solution. A suitable aliquot (usually 20 ml for LiCl and $Ca(H_2PO_4)_2$ extractants, and 10 ml for $NaHCO_3$) containing 5-50 µg S was then transferred to a 50 ml digestion-distillation flask and taken to dryness overnight in a drying oven at 100° C.

The flasks, after removal from the drying oven, were cooled and 1 ml of deionized water was added. Then 4 ml of a reducing mixture (consisting of hydriodic acid, formic acid and hypophosphorus acid, in the ratio of 4:2:1 by volume) was added, the flasks were connected to the modified digestion-distillation apparatus, and the sulfate content determined according to the method of Johnson and Nishita (1952). In this method, sulfate is reduced to H_2S by the reducing mixture and is reacted with zinc acetate to form ZnS. Methylene blue is formed when p-aminodimethylaniline reacts with the H_2S released from ZnS under acid conditions. The reaction is catalyzed by the ferric ion. The optical

density of the resultant solution was measured after 10 minutes, in a Spectronic 20 photoelectric colorimeter using a wave length of 670 mμ. By careful preparation of the reducing mixture and by taking precautions to avoid contamination, the blank determinations seldom indicated that more than 1 μg of S was present.

When the $NaHCO_3$ extractant was used, 1.5 ml of 6 N HCl instead of 1 ml of water was added to the 50 ml flask after oven-drying to neutralize the carbonate prior to addition of the reducing acid mixture. Failure to neutralize the carbonate was shown to reduce the effectiveness of the reducing acids by giving lower values for extractable sulfate.

The pipette method of Kilmer and Alexander (1949) was used for the particle-size analysis of soils. The procedure consisted of destruction of organic matter with hydrogen peroxide, dispersal of the particles with sodium metaphosphate and determination of (1) the clay content (< 2 μ) by pipetting, (2) the sand fraction by sieving through a 300 mesh screen and (3) silt fraction by difference.

The available moisture status of each soil was estimated by determining the percent water by weight retained at 1/3 and 15 atmospheres tension, according to the methods outlined by Richards (1965). The 1/3 atmosphere water retention was determined using a porous ceramic plate in

a pressure cooker, whereas the 15 atmosphere water retention was obtained using a cellulose acetate pressure membrane. The moisture content of samples was determined gravimetrically after oven-drying for 24 hours at 105° C.

Plant analyses

Ryegrass from the greenhouse experiments was dried at 65° C for 48 hours and then ground in a Wiley mill through a 20 mesh screen. Samples were analyzed for total sulfur according to the method of Tabatabai and Bremner (1970c). In this procedure 0.25 g of plant material is digested with 3 ml nitric and 2 ml of 70% perchloric acid in a 100 ml volumetric flask. The digestion is continued for one hour after white fumes of perchloric acid appear in the flask. After cooling, 3 ml of 6 N HCl is added and the flask is made to volume with deionized water. The flasks are inverted several times and then allowed to stand overnight to permit the insoluble plant silica to settle.

Sulfate-S in the Digest was determined by transferring a 10 ml aliquot of the clear supernatant to a 100 ml test tube, adding 10 ml of water and 1 ml of a barium-chloride gelatin reagent, and swirling for several seconds to mix the contents. After 40 minutes the resultant turbidity was measured in a Klett-Summerson photoelectric colorimeter using a blue filter (420 mμ) and a 2 cm light path. The sulfate content of the aliquot taken was obtained by

reference to a standard curve prepared by pipetting into 100 ml volumetric flasks 0, 2, 4, 8, 12 and 16 mls of a 80 µg/ml sulfate solution. Nitric and perchloric acids are added and the procedure as described for the analysis of total S in plant material, followed.

Good reproducibility can be obtained with this method provided some care is exercised in standardizing the preparation and mixing of the gelatin-$BaCl_2$ reagent with diluted aliquot. In particular, the gelatin-$BaCl_2$ reagent, after addition of the $BaCl_2$, should be left to stand at room temperature for at least 2 hours. A shorter standing time results in a lower turbidity with a consequent lower recovery of SO_4-S. It was found necessary also to rigidly control the swirling time after addition of $BaCl_2$. Small differences in the slope of the calibration graph between operators, have been found due to differences in the mixing of $BaCl_2$-gelatin reagent with the diluted aliquot. Because of differences obtained in the slope of the calibration curve between operators, and between days, it was considered necessary to run several SO_4 standards with each series of plant analysis.

Greenhouse Methods

The uptake of nutrients by a test crop grown under greenhouse conditions, on a range of representative soils, is considered to be the most reliable method of obtaining

indices of plant nutrient availability (Hanway and Ozus, 1966). Many different methods have been used under greenhouse conditions to obtain such indices. Basically they all have the same purpose but differ with respect to length of the nutrient uptake period, amount of soil or sand and soil used, test crop and the method of applying basal nutrients.

Methods can be classed as either direct or indirect. In the case of direct methods of assessing plant nutrient availability, as employed by Neubauer and Schneider (1923), Bouldin (1956) and Stanford and DeMent (1957) and Koswara and Hanway (1969), a test crop is grown on a group of soils and the total yield of nutrient in the crop after a given period, provides a good index of nutrient availability. Indirect methods generally employ an internal standard and the indices determined can be expressed as "A" values, where labelled fertilizer is used (Fried and Dean, 1952), "a" values where an estimate of plant available nutrient is made by extrapolating to zero the yield of nutrient curve (Dean, 1954) or "b" values obtained by extrapolating dry matter yield curves back to zero yield (Mitscherlich, 1935).

Some of the more important requirements for the evaluation of nutrient availability in soils using greenhouse methods, have been enumerated by Hanway and Ozus (1966).

In order that the soil sample used, be representative of field soils, they should neither be dried nor modified more than is necessary, nor should any amendments be made to the soil that might affect the availability in the soil of the nutrient being tested. All essential nutrients except that one being studied, should be supplied to the test crop for the duration of the experiment in such a way that they do not influence the availability of the nutrient being studied. Due attention to these requirements was made in the experiments about to be described.

Objectives

Two greenhouse experiments were set up in fall of 1968. The objectives of Experiment 1 were:

1. To obtain indices of plant available sulfur in a range of Iowa soils, for correlation with sulfur extracted by chemical methods.
2. To determine the response of ryegrass to applied sulfate on a range of Iowa soils.

The objective of Experiment 2 was primarily:

1. To determine the effect of air-drying soil on the availability of sulfur to plants.

Design

In Experiment 1, a split plot design was used with 21 soils as whole plots, applied sulfur treatments as sub-plots and five harvests as sub-subplots. The treatments

were replicated three times and consisted of five rates of sulfur, 0, 7.5, 15, 22.5 and 30 ppm S as gypsum, mixed through the soil prior to potting. The experiment was arranged in three blocks, each block containing a complete replicate and occupying a greenhouse bench 3-1/2 x 20 foot. Such a blocking arrangement provided a means of conducting certain greenhouse operations, such as harvesting on a block by block basis. Also, variation due to differences in temperature and light across the greenhouse, can be removed by this blocking arrangement.

In Experiment 2 a split plot design was used, with four sulfur treatments applied to six soils as whole plots, two drying treatments as subplots and three harvests as sub-subplots. There were two replications arranged in two blocks on a 3-1/2 x 18 foot greenhouse bench.

Sand preparation

Silica sand, obtained from the Martin-Marietta Corporation, Clayton, Iowa, was used in the potting technique to be described later. In order to accurately assess the available sulfur supply of the test soils it is necessary to keep the level of sulfur, from sources other than the test soils, at a minimum. Water soluble sulfur in the commercially available silica sand was checked prior to its use in greenhouse experiments. It was determined by shaking 20 g of sand with 40 ml of deionized water over-

night, filtering, transferring a 2 ml aliquot of filtrate to a 50 ml digestion-distillation flask, and analysis for sulfate-sulfur according to the procedure described by Johnson and Nishita (1952). Unwashed silica sand was found to contain 5-10 ppm water soluble sulfur. Treatment of silica sand with dilute 0.5 N HCl, followed by leaching with distilled water until chloride ions could no longer be detected, was effective in reducing the water-soluble sulfur content from 5 ppm to about 1 ppm. A level of 1 ppm water-soluble sulfur was considered to be satisfactory for the greenhouse experiment.

The water-soluble sulfur content of silica sand before and after treatment is shown in Table 3. In addition, analyses for both total S (Tabatabai and Bremner, 1970b) and HI-reducible S (Freney, 1957) were made to further characterize the sulfur status of the silica sand. These results indicate that most of the total sulfur was co-precipitated within the sand grains and would therefore be unavailable to plant roots. The HI-reducible sulfur would represent a fraction of inorganic S which has been removed from the outermost layers of the sand grains.

On the basis of the above tests run on both treated and untreated sand, bulk quantities of sand were treated for use in the two greenhouse experiments. The procedure adopted was as follows:

Table 3. Sulfur content of silica sand

Batch no.	Treatment	H_2O soluble	HI-reducible (ppm S)	Total
1	0.5 N HCl + leaching	1.2	19.2	49.6
2	" "	1.0	14.6	54.3
3	" "	1.2	24.2	48.6
4	Untreated	5.0	-	-

Dry silica sand was saturated with 0.5 N HCl in a glazed earthenware crock and allowed to stand at least 24 hours. The free acid was poured off and the contents of the crock were transferred to a leaching funnel, made from an inverted 4-gallon polyethylene bottle with the base removed. The neck of the funnel contained a heavy wire screen on which was placed a layer of glasswool to retain the sand and yet permit rapid leaching. The sand was then leached with distilled water until a negative test for chloride was obtained. Normally the chloride level of the leachate was down to 1 ppm after 3 hours. The sand was then dried on clear polyethylene film in the greenhouse and stored until required.

Ryegrass in sand culture

Ryegrass has been found to be a suitable greenhouse test crop in nutrient uptake studies (Hanway and Ozus, 1966; Isobe, 1966; Tabatabai and Hanway, 1968; and Koswara and Hanway, 1969) for the following reasons:

1. It germinates easily and grows readily over a wide range of soil characteristics under greenhouse conditions.
2. It can be harvested repeatedly without deleterious effects and is therefore suited for the study of nutrient uptake over an extended period.
3. It is responsive to added nutrients but will survive under conditions of severe deficiency of many nutrients.

For these reasons ryegrass was used in both Experiments 1 and 2. It was established initially in sand culture, and transferred after 40 days to No. 10 cans containing the test soils. The purpose of this step was to develop a vigorous culture of ryegrass, uniform with respect to stand and growth. Such uniform material would tend to minimize differences in plant yield between soils, differences which frequently result from the physical and chemical effects of soils on seedling establishment.

The method employed for establishing the sand cultures was adapted from that of Tabatabai and Hanway (1968) and

is described as follows:

A cardboard ring 5.8 inches in diameter, impregnated with wax (paraffin 2 parts, beeswax 1 part by weight) was placed on a styrofoam plate 9 x 8 inches. The cardboard rings were made from strips of 6-ply posterboard, 19.7 x 1.25 inches, and stapled top and bottom with a 1.25 inch overlap. Acid-washed silica sand (500 g) moistened with 25 ml of deionized water to provide cohesion, was added to each ring and the surface was leveled and lightly compacted. Annual ryegrass, Lolium multiflorum seed (0.6 g/ring), was sown on the leveled sand and covered with a further 200 g dry sand. Sufficient additional water was applied to bring the moisture content of the sand to 19 percent by weight. This water and subsequent waterings was applied to the plate outside the sand culture which thus prevented disturbance of the surface. The sand cultures were covered to prevent loss of moisture, until after emergence.

The ryegrass was sown on August 6, 1968 and emerged three days later. The cultures were watered daily with deionized, distilled water and twice weekly with Hoagland's minus-sulfur solution (Hoagland and Arnon, 1950). This nutrient solution was prepared by mixing from stock solutions 4 ml of M $Ca(NO_3)_2 \cdot 4H_2O$, 6 ml of M KNO_3, 2 ml of M $Mg(NO_3)_2$, 1 ml of M KH_2PO_4, 1 ml of 0.5 percent Fe citrate solution, and 1 ml of a micronutrient solution of the

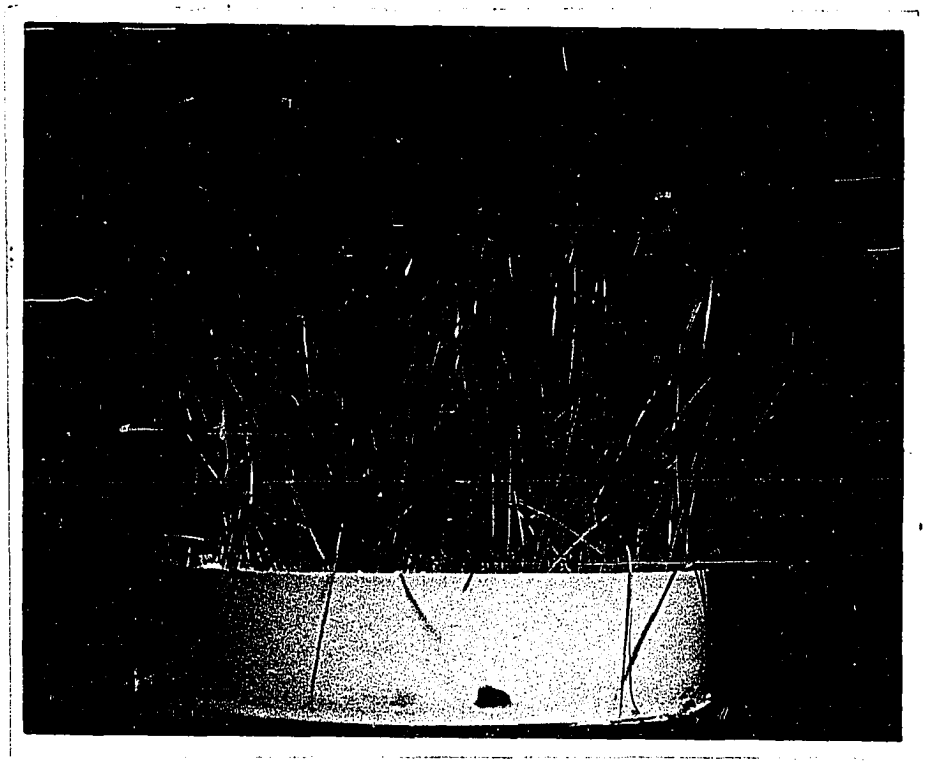
following composition:

Compound	g/liter
H_3BO_3	2.86
$MnCl_2 \cdot 4H_2O$	1.81
$ZnCl_2$	0.22
$CuCl_2 \cdot 2H_2O$	0.08
Na_2MoO_4	0.02

and diluting to 1 liter. During the first three weeks the nutrient solution was applied at half strength, thereafter at full strength. Over the 40 day growing period 168 mg N, 180 mg K and 20.7 mg P were applied to the ryegrass in sand culture.

Two weeks after emergence rather severe symptoms of sulfur deficiency developed and the growth rate of ryegrass was decreased. To correct this deficiency, 0.5 mg of sulfur as $CaSO_4 \cdot 2H_2O$ was applied in the nutrient solution to each culture. The addition of sulfur to the ryegrass was intended to provide sufficient sulfur for the development of a vigorous plant which, at the time of transfer to the test soil, would contain a critical level (0.20 percent) of sulfur. Application of sulfur improved growth and color of the ryegrass and dry matter harvested from the plants prior to transfer, indicated a concentration of 0.16 percent S. A typical example of ryegrass grown in sand culture, one week prior to transfer is shown in Figure 2

Figure 2. Annual ryegrass grown in sand culture, with minus S nutrient solution, one week prior to transfer



and after clipping three days before transfer, in Figure 3.

Treatment application

The equivalent of 1500 g of field moist soil (4 mesh) was preweighed into polyethylene bags. The sulfur treatments were applied on a per pot basis as follows:

The 1500 g soil sample was spread out to a depth of 1/2 inch on clean brown paper and the sulfur treatments were applied in solution as $CaSO_4 \cdot 2H_2O$ to the surface of the soil using a plastic syringe with a fine delivery nozzle. The rates used and the weights of sulfur added per pot, are shown in Table 4. Mixing of the applied $CaSO_4$ solution throughout the soil was further achieved by rolling the soil back and forth on the paper.

Table 4. Rates of sulfur applied in experiment 1/68

Treatment no.	Rate applied (ppm S)	Rate/pot (mg S)	$CaSO_4$/pot (mg)	S soln./pot (ml)[a]
1	0	0	0	0
2	7.5	11.25	60.53	30
3	15	22.50	121.05	60
4	22.5	33.75	181.57	90
5	30	45	242.76	120

[a]This solution contains 2.0175 g $CaSO_4 \cdot 2H_2O$/liter.

Figure 3. Annual ryegrass grown in sand culture, with minus S nutrient solution, three days before transfer (all plants very sulfur deficient)

Because the solubility of $CaSO_4 \cdot 2H_2O$ is somewhat low (2.41 g/L), the amount of solution that was needed to apply the 22.5 and 30 ppm S rate was somewhat excessive. On those soils whose field moisture content approached field capacity, it was found necessary to reduce the field moisture content by partial air-drying before applying the sulfate solution.

Potting of soils

The procedure used to set up the pot cultures for both Experiments 1 and 2 was similar to that described by Tabatabai and Hanway (1968). In Experiment 1 sufficient acid-washed silica sand (ca. 1325 g) was added to each pot (No. 10 metal cans lined with double polyethylene bags), to bring the combined weight to 1600 g. The surface of the sand was leveled after the addition of 100 ml deionized water. Then a 6-1/2 inch length of 1/2 inch diameter plastic garden hose was inserted into a centrally-located hole in the sand made with a No. 13 cork borer. The hose provided a convenient means of adding nutrients directly to the basal sand layer.

The treated soils (equivalent to 1500 g oven dry soil) were added and uniformly consolidated to give a bulk density of 0.95 for silt loams and silty clay loams, and 1.20 for soils of coarser texture. In order to keep the upper surface of the coarse-textured soils at the same depth

below the pot rim as the fine textured soils, 1875 g rather than 1325 g of silica sand was placed below the soil layer. When all soils were potted, the ryegrass in sand culture was transferred bodily to the pots. A hole was first cut in the center of the sand culture with a No. 13 cork borer, to accommodate the plastic tube. The sand culture was then transferred to a heavy cardboard disc which had a slot running from the rim to the center. The culture and disc were then centrally positioned over the access tube, the slotted disc removed, and the sand culture lowered onto the soil surface. The cardboard ring was removed at this stage. This procedure brought the upper surface of the sand culture 3/4 inch below the rim of the can. In Experiment 2 less basal sand was used which brought the upper surface of the sand culture to within 1-1/4 inches of the rim of the can. The rim of the can in Experiment 2 therefore provided a convenient cutting height for all subsequent harvesting operations. The arrangement of soil, sand, and ryegrass plants in the pots is shown in Figure 4 and the volume and weight of these components in Table 5. Transfer of ryegrass to the pots was completed in three days in Experiment 1, and in one day in Experiment 2.

Watering

Following transfer of the ryegrass to the soils, all pots were weighed and sufficient deionized water was added

Figure 4. Section through a pot from Experiment 1/68 to show the arrangement of basal sand, access tube to supply nutrients, and the test soil (the test soil shown, is Weller 18 to 24 inches)

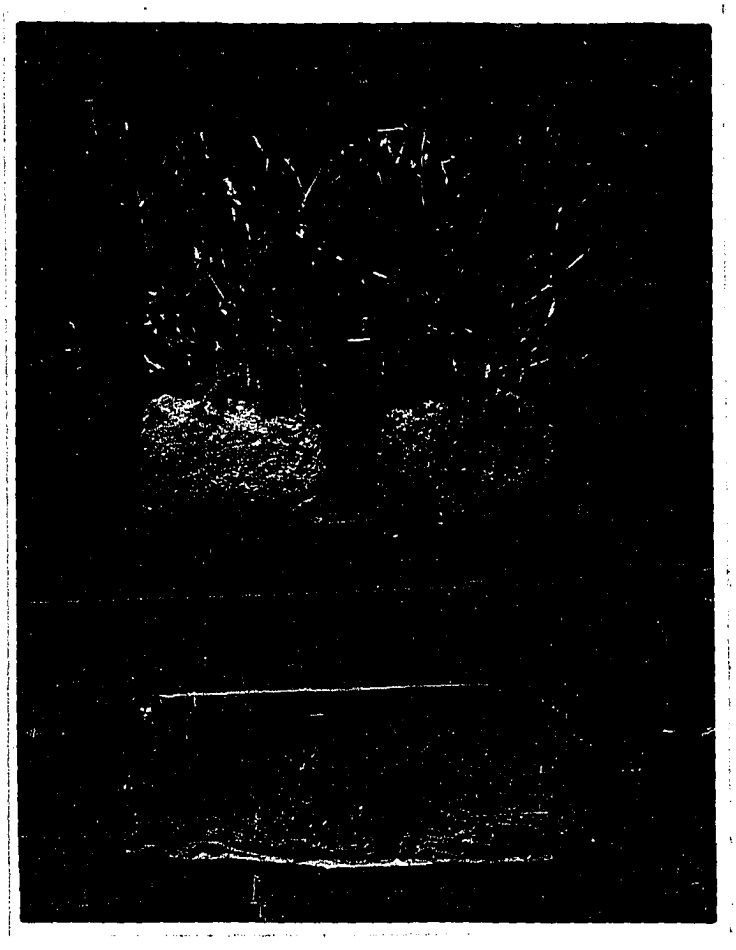


Table 5. Soil and sand used in pot cultures

Experiment	Component	Fine textured soils Weight (g)	Fine textured soils Depth (in)	Coarse textured soils Weight (g)	Coarse textured soils Depth (in)
1	Clearance	-	3/4	-	3/4
	Upper sand	700	1	700	1
	Soil	1500	3-1/2	1500	2-3/4
	Basal sand	1325	1-3/4	1875	2-1/2
	No. 10 can	275		275	
	Total	3800	7	4350	7
2	Clearance	-	1-1/4	-	1-1/4
	Upper sand	700	1	700	1
	Soil	1500	3-1/2	1500	3
	Basal sand	1005	1-1/4	1250	1-3/4
	No. 10 can	275		275	
	Total	3480	7	3725	7

to raise the moisture content of the soil and sand in the pot to an upper limit, favorable for plant growth. Subsequent watering throughout the experiment was designed to maintain the moisture content of the pot between 50 percent available moisture, the lower limit, and a predetermined upper limit.

The upper and lower limits for soil moisture were based on the percent moisture retained at 1/3 and 15 atmospheres tension for each soil (see Table 6). In both Experiments 1 and 2, representative values of 25 percent and 12 percent for field capacity and wilting percentage, respectively, were adopted for the fine textured soils, and 15 percent and 5 percent for the coarse-textured soils. A moisture holding capacity of 12 percent by weight was adopted for the silica sand and this moisture content was also used as the upper limit when watering the sand cultures. The moisture added to raise the fine-textured soils and sand in the pot to the upper limit consisted of:

Water to bring 1500 g soil to 25 percent moisture content, plus water to bring 2025 g silica sand to 12 percent moisture content. In calculating available moisture per pot, that above 12 percent in fine-textured and above 5 percent in coarse-textured soils was considered available, while for silica sand all moisture held was considered available. Tests showed that the moisture retained by the

sand, at a suction of 15 atmospheres, was approximately 0.2 percent.

Initially, daily watering was necessary, but with reduced growth resulting from sulfur deficiency, watering was required less frequently as the experiment progressed. The weighing of a few representative pots provided a good estimate of the moisture status of the pot and the quantity of water to be applied, at each watering.

Maintenance of experiments

The ryegrass was harvested every 5 to 6 weeks by cutting 1-1/4 inches above the sand surface. One replicate was harvested per day and replicates were harvested in the same order at each cutting. Basal nutrients were applied immediately following each harvest and again 2-1/2 weeks later so as to apply a total of 120 mg N, 15.5 mg P and 136 mg of K between harvests. The nutrient solution was identical in composition to that described for the sand cultures, except that in order to reduce the frequency of application it was applied at five times normal strength. The micronutrient component of the nutrient solution was omitted after the first harvest, because it was considered that the soils would be adequately supplied with these elements. All nutrient solution was applied to the basal sand layer by way of the plastic hose. In effect, the pot culture consisted of a split nutrient medium with plant

roots largely dependent on the basal sand layer for all nutrients except sulfur, and dependent on the soil almost exclusively for their sulfur supply. Experiment 1 ran from September 16, 1968 to April 10, 1969, when it was terminated after the fifth harvest of ryegrass. By this time, the ryegrass was showing sulfur deficiency symptoms on nearly all soils at all rates of applied sulfur, except in some cases at the 30 ppm S rate. On three soils, Monona 0-6 inches, Albaton 0-6 inches and Weller 18-24 inches, dry matter yields were being maintained prior to harvest 5, even at low rates of applied S. Consequently three treatments (0, 15 and 30 ppm S) on each of these soils were continued for a further three harvests. Details concerning harvest dates, time of application of nutrient solution and the amount of nutrients applied are given in the Appendix.

Experiment 2 was terminated after three harvests when sulfur deficiency was apparent at the lower rates of applied sulfur.

In both experiments a representative soil sample was taken from each pot a few days after the final harvest. These samples were stored moist in a cool room maintained at 3° C. In Experiment 1 the stubble was harvested separately, dried at 65° C for 48 hours and weighed.

RESULTS AND DISCUSSION

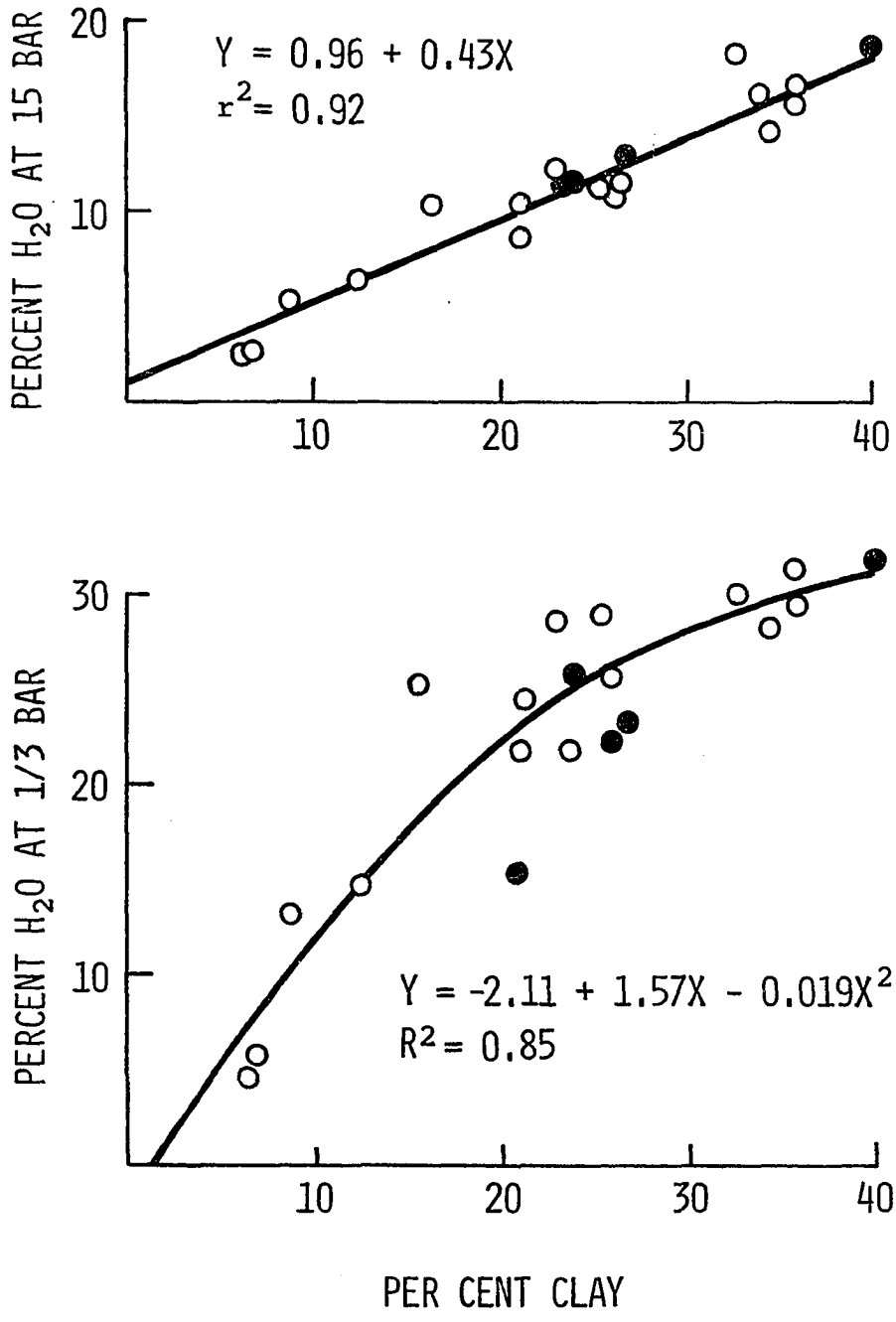
Soil Characteristics

Some physical and chemical properties of the soil samples collected for the greenhouse experiment 1/68 and subsequent laboratory studies are given in Tables 37 and 38 of the Appendix.

Percent clay ranged from 6.3 percent in Thurman sand to 40.1 percent in the 18-24 inch depth of Webster clay loam. Clay content increased in the loess soils of southwest Iowa with increasing distance from the loess source (Hamburg < Ida < Monona < Marshall < Sharpsburg). This is consistent with the relationships described by Ruhe (1969). The percent sand was low in all loess soils and, in the sequence of soils from southwest Iowa, decreased from 7.7 percent in the Hamburg soil to 1.5 percent in the Marshall and Sharpsburg soils. Other soils contained higher percentages of sand with a maximum of 86 percent in Thurman sand.

Moisture retention at both 1/3 bar and 15 bars tension was closely correlated with percent clay in the soil (Figure 5). The relationship between percent clay and moisture retained at 15 bars was linear, whereas that between clay and the moisture retained at 1/3 bar was curvilinear. Thus, as the clay content increased the water retained at 1/3 bar increased at a decreasing rate.

Figure 5. Relationship between percent clay in the soil and moisture held at 1/3 and 15 bars tension (In this and subsequent figures, open circles represent surface soils and solid circles represent subsoils)


Y = 0.96 + 0.43X
r² = 0.92
PERCENT H₂O AT 15 BAR
20
10
10
20
30
40
Y = -2.11 + 1.57X - 0.019X²
R² = 0.85
PERCENT H₂O AT 1/3 BAR
30
20
10
10
20
30
40
PER CENT CLAY

Organic carbon contents in the surface soils ranged from 0.11 percent in Thurman sand to 2.8 percent in Webster clay loam (Table 38). Soil pH varied from 5.2 to 8.3. Large differences in available N, P and K were found between soils.

In Table 38 three sets of values are given for available nitrogen, viz., anaerobic NH_4-N (Waring and Bremner, 1964) which is an index of the soils capacity to mineralize nitrogen; initial NO_3-N which is the amount of NO_3-N present in the soil at the time of sampling; and available N which is the amount of NO_3-N plus NH_4-N present at the time of sampling. In surface soils anaerobic NH_4-N varied from 6 pp2m in Thurman sand to 105 pp2m in Ida silt loam. Low values were characteristic of sands and subsoils, whereas the three highest values came from soils which were either in meadow or in permanent grassland. The NH_4-N plus NO_3-N (available N) content of soils varied from 23 to 235 pp2m and, as shown later, these differences were considered responsible for differences in dry matter yields of ryegrass in the first harvest of the greenhouse experiment 1/68. Most of the available N was present as NO_3-N, and these high levels of N were probably associated with the use of high rates of N fertilizer on the previous crop. Both available phosphorus and exchangeable potassium showed a wide range of values. Available

phosphorus ranged from 7 pp2m on Hamburg silt loam to 98 pp2m on Albaton silty clay loam, and exchangeable potassium ranged from 22 to > 1000 pp2m. Exchangeable potassium was low in subsoils and in soils derived from glacial till and generally high in soils formed on loess.

Over all, the soils showed wide variations in both physical and chemical characteristics, a feature which was desirable in a study of this kind.

Laboratory Study

Forms of sulfur

The 16 surface soils and 5 subsoils were analyzed for total, HI-reducible and carbon-bonded sulfur and results are given in Table 6. Linear correlations between organic carbon and forms of soil sulfur are given in Table 7.

Total S ranged from 68 to 452 ppm with a mean of 249 ppm S for surface soils and 140 ppm S for subsoils. These values are of the same order as those found in Australian black earths and soils formed on basalt (Williams and Steinbergs, 1958; 1962). They are also similar to total S values of New South Wales soils which ranged from 38 to 545 ppm with a mean of 188 ppm (Spenser and Freney, 1960). The values reported for total S are less than those found in Minnesota soils by Evans and Rost (1945). They found that the total content of six chernozems ranged from 412 to 552 ppm S and nine black prairie soils ranged from 277

Table 6. Organic carbon and forms of sulfur in soils

Soil type	Lab. no.	Organic C %	Total S	HI-reducible S[a]	Carbon-bonded S[a]
			ppm		
		Surface soils			
Hamburg	4	2.06	279	168 (60)	15 (5)
Hagener	3	0.48	78	42 (54)	7 (9)
Webster	2	2.80	336	179 (53)	30 (9)
Thurman	15	0.16	68	36 (53)	3 (4)
Dorset	16	1.62	168	82 (49)	10 (6)
Sharpsburg	8	1.57	264	148 (56)	25 (10)
Fayette	13	1.19	203	112 (55)	28 (14)
Clarion	1	2.10	283	162 (57)	20 (7)
Tama	12	1.88	241	143 (59)	21 (9)
Sarpy	11	1.37	211	101 (48)	19 (9)
Marshall	7	1.52	292	177 (61)	24 (8)
Grundy	9	2.30	289	164 (57)	30 (10)
Albaton	10	1.69	452	209 (46)	24 (5)
Ida	5	1.07	300	163 (54)	15 (5)
Weller	14	1.32	189	96 (51)	15 (8)
Monona	6	1.51	333	184 (55)	26 (8)

[a]Percent of the total S given in brackets.

Table 6. (Continued)

Soil type	Lab. no.	Organic C %	Total S	HI-reducible S[a]	Carbon-bonded S[a]
			ppm		
		Subsoils			
Clarion	17	0.70	160	115 (72)	9 (6)
Webster	18	1.03	110	67 (61)	5 (5)
Fayette	20	0.18	85	70 (82)	3 (4)
Monona	19	0.45	210	155 (74)	8 (4)
Weller	21	0.38	135	95 (70)	5 (4)
Mean surface soils		1.54	249	135 (54)	20 (8)
Mean subsoils		0.54	140	100 (72)	6 (4)

Table 7. Correlations between organic carbon and sulfur fractions in soils

	Correlation coefficients r[a]			
	Organic C	Total S	HI-reducible S	C-bonded S
Organic C	1.000			
Total S	.734	1.000		
HI-reducible	.674	.952	1.000	
C-bonded S	.804	.797	.674	1.000

[a]All correlations significant at 1 percent level.

to 669 ppm S.

Total sulfur was significantly correlated with organic carbon r = 0.734 (Table 7). Close relationships between total S and organic C have been reported by many workers (Donald and Williams, 1954; Walker and Adams, 1958; Harward et al., 1962) from which they have inferred that most of the sulfur, in the surface horizons of soils of humid regions, is in the organic form.

HI-reducible sulfur is believed to consist of sulfated polysaccharides, phenolic sulfates, choline sulfate plus some inorganic sulfate (Freney, 1967). In this study it accounted for an average of 54 percent of the total sulfur in surface soils and 72 percent in subsoils. These results

are similar to those obtained by Freney (1967) who found in Australian soils, an average of 52 percent of the total sulfur present as organic sulfates, 7 percent as inorganic sulfur and the remaining 41 percent as carbon-bonded sulfur. HI-reducible sulfur is shown, in Figure 6 and Table 7, to be very highly correlated with total sulfur.

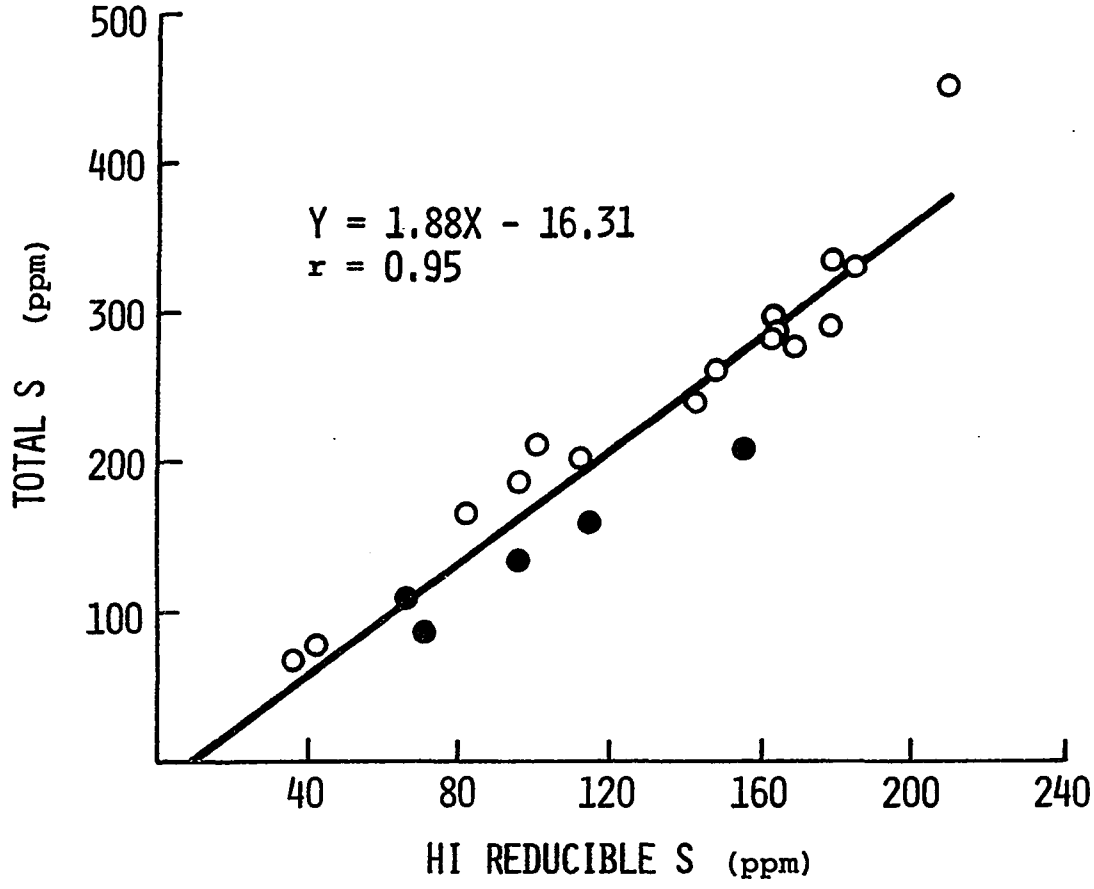
Carbon-bonded sulfur ranged from 3 to 30 ppm and accounted for an average of 8 percent of the total sulfur in surface soils and 4 percent in subsoils. In Canadian soils, Lowe and DeLong (1963) found that carbon-bonded sulfur amounted to 12-35 percent of the total sulfur in mineral soils and 47-58 percent in organic soils. Carbon-bonded sulfur was significantly correlated with total sulfur ($r = 0.797$) and with organic carbon ($r = 0.804$) (Table 7).

Sulfate sulfur

Three different extractants were used to extract fractions of inorganic sulfate which probably included some labile organic sulfate also, in order to obtain indices of plant available sulfur. The extractants used were: 0.1 M LiCl, $Ca(H_2PO_4)_2$ solution containing 500 ppm P, and 0.5 M $NaHCO_3$. Extractions were made on the 16 surface soils and 5 subsoils in both a field moist (FM) and an air-dry (AD) state, at soil to extractant ratios of 1:5 and 1:10.

The complete data for this investigation are shown in Table 39 of the Appendix. An analysis of variance of the

Figure 6. Relationship between HI-reducible sulfur and total sulfur in soils


500
400
300
200
100
TOTAL S (ppm)
Y = 1.88X - 16.31
r = 0.95
40
80
120
160
200
240
HI REDUCIBLE S (ppm)

data is given in Table 8 which shows that the effects of soils, extractants, drying, and the soil:extractant ratio on the amount of sulfate sulfur extracted, were all highly significant.

The mean level of sulfate sulfur removed by each extractant from each soil is shown in Table 9, averaged across the mean for drying and soil to extractant ratio. The soils are listed in order of increasing sulfur availability, based on the yield of sulfur in ryegrass corrected for S supplied in silica sand, grown in the no sulfur treatment of the greenhouse experiment 1/68.

There were large differences among soils in the amount of sulfate S extracted. As shown by the means for the surface soils and subsoils LiCl and $Ca(H_2PO_4)_2$ solutions extracted about the same amount of sulfate sulfur, whereas $NaHCO_3$ extracted about three times as much as did either of the other two. The difference between sulfate sulfur extracted by LiCl and $Ca(H_2PO_4)$ was nonsignificant. Values ranged from 2 to 12 ppm sulfate S extracted with LiCl, and from about 2 to 16 ppm sulfate S with the $Ca(H_2PO_4)_2$ extractant. With the $NaHCO_3$ solution, values ranged from 8 to 40 ppm sulfate sulfur. The sandy soils Hagener loamy sand and Thurman sand, gave the lowest values of sulfate S extracted with LiCl and $Ca(H_2PO_4)_2$. The soil sample which gave the highest value with either LiCl or $Ca(H_2PO_4)_2$ was

Table 8. Analysis of variance of extractable sulfur in soils

Source of variation	df	Mean square	F[a]
Soils	20	259.0283	148.60**
Extractant	2	7311.7930	4194.68**
Soil x extractant	40	122.0061	69.99**
Drying	1	243.8634	139.90**
Soil x drying	20	5.8576	3.36**
Extractant x drying	2	4.7623	2.73
Ratio (Soil:extractant)	1	122.5003	70.28**
Soil x ratio	20	2.3094	1.33
Extractant x ratio	2	12.5521	7.20**
Drying x ratio	1	0.0248	0.01
Error	142	1.7431	
Total	251		

[a]In this and subsequent tables of this dissertation, ** and * will be used to denote statistical significance at the 1 percent and 5 percent levels respectively.

Table 9. Effect of extractant on sulfate sulfur removed from soils[a]

Soils	Lab. no.	Sulfate sulfur (ppm) extracted by ·1 M LiCl	Sulfate sulfur (ppm) extracted by $Ca(H_2PO_4)$ soln.	Sulfate sulfur (ppm) extracted by ·5 M $NaHCO_3$	Yield of S in control plants (mg S/kg soil)
			Surface soils		
Hamburg	4	3.8	2.9	11.4	0.7
Hagener	3	2.9	2.6	12.4	1.3
Webster	2	4.9	5.4	20.5	5.2
Thurman	15	3.6	2.2	8.3	5.3
Dorset	16	5.9	5.2	16.6	5.3
Sharpsburg	8	4.9	6.2	34.0	5.4
Fayette	13	4.3	5.7	30.3	5.7
Clarion	1	6.4	7.8	39.3	6.5
Tama	12	6.4	6.1	32.1	6.8
Sarpy	11	4.1	4.4	7.9	7.2
Marshall	7	8.9	9.4	32.2	7.5

[a]Soils in this and subsequent tables have been arranged in order of increasing yield of sulfur in ryegrass adjusted for silica sand over five harvests from the no sulfur treatment in Experiment 1/68.

Table 9. (Continued)

Soils	Lab. no.	Sulfate sulfur (ppm) extracted by			Yield of S in control plants (mg S/kg soil)
		.1 M LiCl	$Ca(H_2PO_4)$ soln.	.5 M $NaHCO_3$	
Grundy	9	8.0	7.0	36.4	10.3
Albaton	10	8.8	8.9	13.8	11.4
Ida	5	8.2	6.6	16.2	12.4
Weller	14	8.6	5.6	27.3	14.4
Monona	6	10.3	10.4	31.8	23.5
			Subsoils		
Clarion	17	5.3	7.5	32.8	3.5
Webster	18	6.2	5.8	8.6	4.5
Fayette	20	4.8	6.5	13.4	5.4
Monona	19	6.3	5.1	19.0	9.1
Weller	21	12.2	15.6	31.1	25.9
Mean surface		6.3	6.0	21.2	8.1
Mean subsoil		7.0	8.1	21.0	9.7

the 18-24 inch depth of Weller silt loam, which incidentally had the highest clay content (40.1 percent) and the lowest pH (5.2). Obviously the large F value for extractants (Table 8) was due, almost entirely, to differences between the $NaHCO_3$ extractable S and the amount of S extracted by the other two extractants. Compared with the LiCl and $Ca(H_2PO_4)_2$ extractants, $NaHCO_3$ gave highly colored extracts which were no doubt due to a solubilizing effect of the alkaline $NaHCO_3$ solution on soil organic matter. However, there did not appear to be any relationship between color of the $NaHCO_3$ solution after extraction and the amount of sulfate sulfur extracted. For example, the $NaHCO_3$ extract from Sarpy loam was the color of molasses but had the lowest sulfate sulfur value of all soils.

A highly significant soil by extractant interaction indicates that the difference between the $NaHCO_3$ solution and the other two extractants in the amount of sulfate sulfur extracted was not consistent from soil to soil. Thus, over all soils, the relationship was about 3:1 but it ranged from 1.6:1 in the Albaton soil to 5.5:1 in the Clarion soil.

Drying the soil increased the sulfate sulfur extracted by all three extractants (Table 39 of the Appendix and summarized in Table 10). The average drying effect was of the order of 1-2 ppm S for the LiCl and $Ca(H_2PO_4)_2$ extract-

Table 10. Effect of air-drying and soil:extractant ratio on the amount of sulfate sulfur extracted[a]

Drying condition	Sulfate sulfur (ppm) extracted by					
	·1 M LiCl		$Ca(H_2PO_4)$		·5M $NaHCO_3$	
	1:5	1:10	1:5	1:10	1:5	1:10
Field moist	5.2	6.0	5.4	6.0	20.0	22.8
Air-dry	6.6	7.9	6.9	7.9	23.0	24.8

[a]L.S.D. 5% = 0.81 ppm.

ants and 2-3 ppm S for the $NaHCO_3$ solution. However, the extractant by drying interaction failed to reach significance at the 5 percent level. Very little change occurred on drying the Dorset soil. Unfortunately this soil had been screened and air-dried in Minnesota prior to shipment which also accounted for its rather better sulfur-supplying power than recent studies by Seim et al. (1969) would indicate. Probably the Thurman sand from Nebraska had also been dried prior to shipment, although the surface few inches of such a coarse-textured soil, would become depleted of moisture quite rapidly in summer, in the absence of rain. A highly significant drying by soil interaction (Table 8) indicates that the effect of drying on the release of sulfate sulfur was much greater on some soils than others.

Increasing the ratio of soil to extractant, signifi-

cantly increased the amount of sulfate sulfur extracted. The analysis of variance, Table 8, shows that the effect of increasing the extractant ratio from soil to soil was fairly consistent. However, over all soils, increasing the ratio from 1:5 to 1:10 resulted in a greater increase in sulfate sulfur extracted with the $NaHCO_3$ extractant, than with the other extractants (Table 10). This is the basis of the highly significant extractant by ratio interaction (Table 8).

Effect of pH of the phosphate extractant Acid subsoils, containing appreciable Fe and Al oxides and kaolinitic clays, have the capacity to adsorb considerable amounts of inorganic sulfate (Ensminger, 1954; Chao et al., 1962b; and Fox et al., 1964b). The additional sulfate sulfur extracted by a solution of KH_2PO_4 or $Ca(H_2PO_4)_2$ compared with that extracted by NaCl, $CaCl_2$ or LiCl has been considered to give a measure of adsorbed sulfate (Ensminger and Freney, 1966). In this study $Ca(H_2PO_4)_2$ extracted more sulfate sulfur than LiCl in about half the soils, while on the remaining soils, the reverse was the case. In the Weller subsoil, which was the only strongly acid subsoil used in this study, an additional 4 ppm of sulfate sulfur was extracted using $Ca(H_2PO_4)_2$. However, less sulfate was extracted with $Ca(H_2PO_4)_2$ than with LiCl from the Weller surface soil, which also was strongly

acid (pH 5.2).

Some additional analyses were made to test the effectiveness of the $Ca(H_2PO_4)_2$ solution as an extractant for adsorbed as well as water soluble sulfur. A solution of $Ca(H_2PO_4)_2$ containing 500 ppm P has a pH of 3.3, whereas the pH of 0.1 M LiCl is 6.2. Since sulfate adsorption is increased by reducing the pH of the equilibrating solution (Kamprath et al., 1956), it was expected that the use of a strongly acid extractant would, by increasing sulfate adsorption, reduce the amount of sulfate sulfur desorbed. Reisenauer (1967) examined the effect of varying the pH of the soil-extractant suspension on the amount of sulfate extracted, while keeping the anion concentration constant. Within the range of pH 5.5 to 7.2 he found that pH had little influence on the sulfate S extracted. Below pH 5.0 however, the amount of sulfur extracted, dropped sharply.

In the present study five soils, including the acid Weller subsoil, were extracted with a KH_2PO_4 solution containing 500 ppm P that had been adjusted to pH 3.3, 4.6 and 6.7. At the same time soils were also extracted with 0.1 M LiCl and the $Ca(H_2PO_4)_2$ solution used in the main laboratory study. Extractions were made on undried soils at a soil to extractant ratio of 1:5. The results given in Table 11, show that varying the pH of the extractant

Table 11. Effect of pH of extractant on sulfate sulfur extracted

Soil	Depth (in)	pH	Extractable SO_4-S (ppm)				
			LiCl pH 6.2	$Ca(H_2PO_4)_2$ pH 3.3	KH_2PO_4 pH 3.3	4.6	6.7[a]
Weller	0-6	5.2	5.8	3.6	4.4	3.8	4.3[b]
Fayette	0-6	6.4	3.6	4.7	5.1	5.3	5.8[b]
Clarion	0-6	6.1	4.6	4.9	5.3	5.2	6.3[b]
Marshall	0-6	7.5	7.4	7.6	8.4	7.5	8.3
Weller	18-24	5.2	10.4	15.2	15.4	15.0	15.6
Mean			6.4	7.2	7.7	7.4	8.1

[a]Filtered through 42 Whatman to reduce cloudiness.

[b]Extracts very cloudy.

had very little effect on the amount of sulfate extracted. The pH of soil-extractant suspension was not measured and the differences in pH in the soil suspension would probably have been much smaller than those in the extractants alone.

On the Weller subsoil the phosphate extractant regardless of pH, extracted much more sulfate-sulfur than did LiCl. Clearly this subsoil contains at least 4-5 ppm of adsorbed sulfate S extractable by $Ca(H_2PO_4)_2$. The results indicate that small amounts of adsorbed sulfate may be present also in the Fayette and Clarion surface soils.

A depression in the sulfate extracted in the Weller surface soil suggests that there was little or no adsorbed sulfate present in this soil and that the acidifying effect of the $Ca(H_2PO_4)_2$ reduced the sulfate extracted due to an increase in sulfate adsorption capacity.

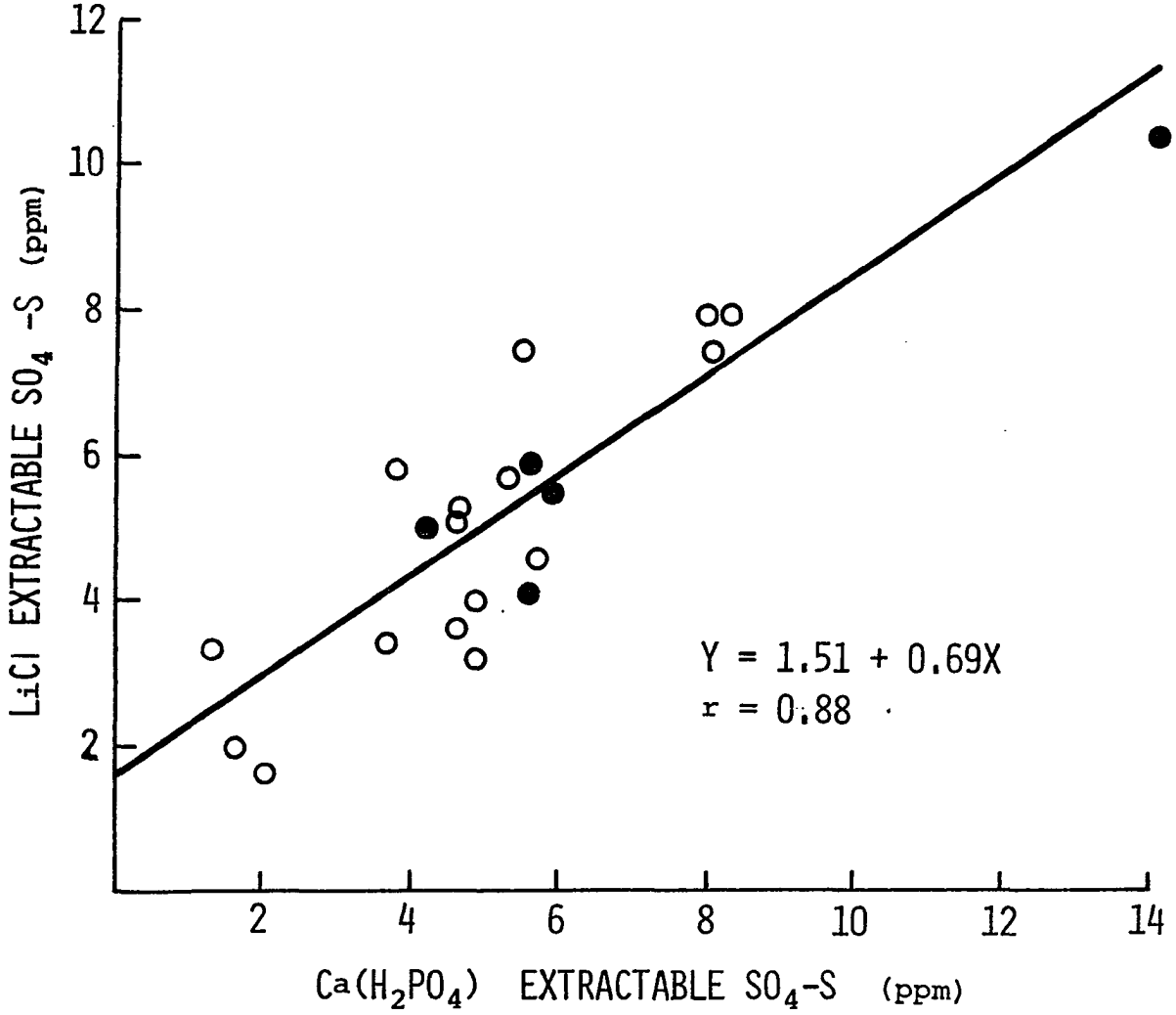
Correlation between laboratory indices of available sulfur

The correlation matrix for the relationship between the different laboratory analyses of available sulfur is given in Tables 40 and 41 of the Appendix. Correlations between the amount of sulfate sulfur extracted from dried and field moist soils within an extractant, were very high ($r > 0.900$). Correlations between sulfate sulfur extracted at a soil:extractant ratio of 1:5 and at 1:10 were even higher ($r > 0.940$) when the drying condition and the extractant was the same.

The amounts of sulfate sulfur extracted by LiCl and by $Ca(H_2PO_4)_2$ were highly correlated. Correlations were highest between extractants when the drying treatments were the same. For example, at a 1:5 ratio, the correlation coefficient for sulfate sulfur extracted by LiCl and that extracted by $Ca(H_2PO_4)_2$ from moist soils was 0.88 (Figure 7) and from dried soils was 0.84. Correlations between sulfate sulfur extracted by one extractant and another were little affected by the soil:extractant ratio.

Little relationship appears to exist between the amount

Figure 7. Relationship between sulfate sulfur extracted by $Ca(H_2PO_4)_2$ and 0.1 M LiCl, on field moist soils


12
10
8
6
4
2
LiCl EXTRACTABLE SO_4 -S (ppm)
2
4
6
8
10
12
14
$Ca(H_2PO_4)$ EXTRACTABLE SO_4-S (ppm)
Y = 1.51 + 0.69X
r = 0.88

of sulfate-sulfur extracted by the LiCl or $Ca(H_2PO_4)_2$ extractants and that extracted by $NaHCO_3$. Correlations made between sulfate sulfur extracted by LiCl at a 1:5 ratio on field moist soils and by $NaHCO_3$ on both dried and undried samples at either drying treatment, were not significant (for significance at the 5 percent level an $r > 0.43$ was required). However, sulfate-sulfur extracted by LiCl on dried samples at either 1:5 or 1:10 ratios, was significantly correlated with $NaHCO_3$ extractable sulfate. Correlation coefficients ranged from 0.49 to 0.56. The better relationship obtained with dried samples suggests that the additional sulfate sulfur extracted by the LiCl solution after drying, was extracted by $NaHCO_3$ regardless of drying treatment. A similar relationship existed between sulfate sulfur extracted by $Ca(H_2PO_4)_2$ and $NaHCO_3$ extractable sulfate. Sulfate sulfur extracted by $Ca(H_2PO_4)_2$ from dried soils was highly significantly correlated with $NaHCO_3$ extractable sulfate ($r = 0.604$ to 0.647).

Correlation coefficients were also computed between the soil sulfur fractions ("HI-reducible" S, carbon-bonded S and total S) and sulfate sulfur extracted with LiCl, $Ca(H_2PO_4)_2$ and $NaHCO_3$. However, in general there was very little relationship; there was a correlation between sulfate sulfur extracted by LiCl on a dried sample and HI-reducible sulfur ($r = 0.46$ and 0.47). Sulfate sulfur extracted with

$NaHCO_3$ was significantly correlated with carbon-bonded sulfur (r = 0.44 to 0.59) and when the calcareous soils were omitted from the relationship, $NaHCO_3$ extractable sulfate sulfur was very highly correlated with HI-reducible S and total sulfur (Figures 8 and 9). Why calcareous soils should contain relatively less $NaHCO_3$ extractable sulfate sulfur, at a given level of HI-reducible sulfur or total sulfur than soils with an acid to neutral reaction is not known. Perhaps solublization with subsequent leaching of part of the organic sulfur occurs during soil formation under alkaline conditions in calcareous soils. The anomalous Webster soil (pH 6.3), which was included with the calcareous soils, probably formed under calcareous conditions during which time losses of some organic sulfur occurred. Drainage and cultivation of these soils during the past century could have leached the free $CaCO_3$ from the surface. Depth samples taken in May, 1969 from this Webster soil for the determination of extractable sulfate sulfur, pH and available phosphorus (Table 46) showed a pH of 6.6 in the top 12 inches and free carbonates below this depth.

Greenhouse Studies

Experiment 1/68

This experiment was designed to assess the plant response obtained from applied sulfur on some Iowa soils,

Figure 8. Relationship between HI-reducible sulfur and sulfate sulfur extracted by 0.5 M $NaHCO_3$, on field moist soils (pH values are given for calcareous soils and the relationship on these soils is shown in the lower regression)

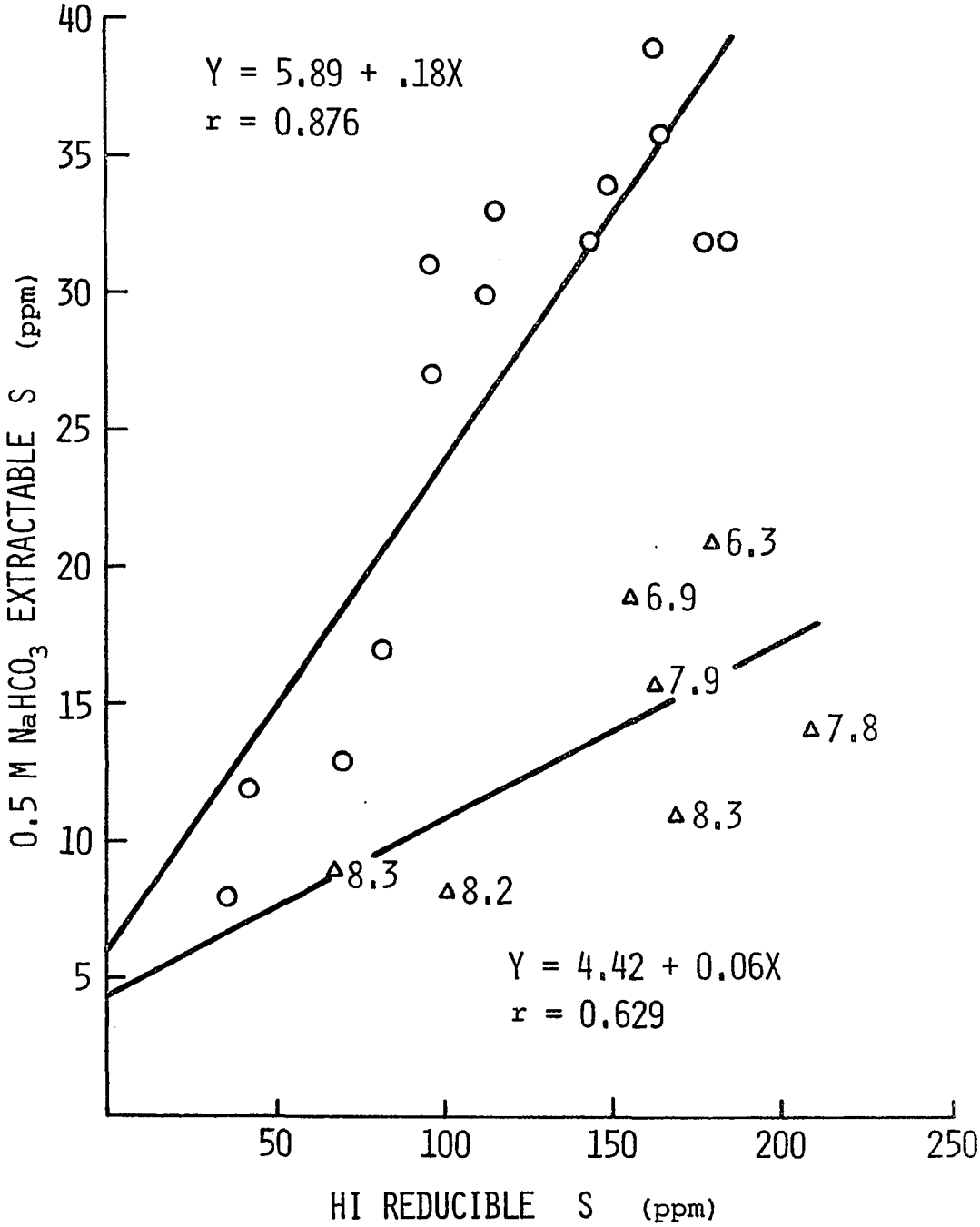
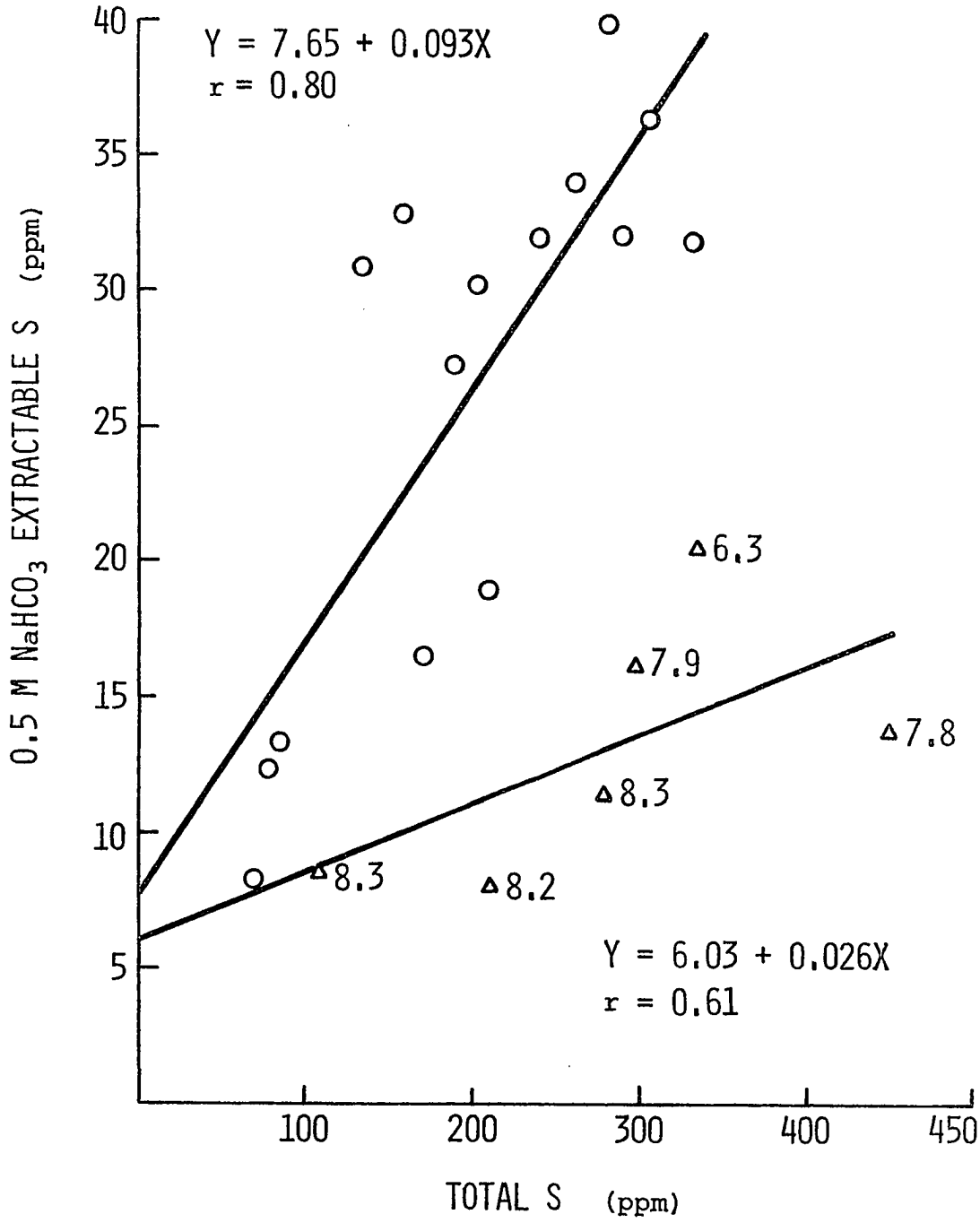

Y = 5.89 + .18X
r = 0.876
Y = 4.42 + 0.06X
r = 0.629
6.3
6.9
7.9
7.8
8.3
8.3
8.2
40
35
30
25
20
15
10
5
50
100
150
200
250
0.5 M NaHCO3 EXTRACTABLE S (ppm)
HI REDUCIBLE S (ppm)

Figure 9. Relationship between total sulfur and sulfate sulfur extracted by 0.5 M $NaHCO_3$, on field moist soils (pH values are given for calcareous soils and the relationship on these soils is shown in the lower regression)


Y = 7.65 + 0.093X
r = 0.80
Y = 6.03 + 0.026X
r = 0.61
6.3
7.9
7.8
8.3
8.3
8.2
40
35
30
25
20
15
10
5
100
200
300
400
450
0.5 M NaHCO3 EXTRACTABLE S (ppm)
TOTAL S (ppm)

and to obtain indices of the available sulfur status of these soils.

Ryegrass plants, growth in sand culture, were transferred to the soils after 42 days growth in a minus-S nutrient solution. At the time of transfer, the ryegrass was sulfur deficient (Figure 3) but within seven days, the plants had developed normal color on all soils.

Dry matter yields

Differences in growth between soils became apparent within two weeks of transfer, and, within three weeks a response to sulfur was observed on the Hamburg soil. In general, ryegrass growth was poorer on subsoils than on the majority of surface soils. The first harvest was made 31 days after transfer when growth on the better soils was 6 to 8 inches in height. Dry matter yields for the first harvest are shown in Table 42, of the Appendix.

An analysis of variance of dry matter yields for the first harvest, Table 12, showed that the effects of soil and of sulfur applied were highly significant. A low mean square for blocks indicated that growing conditions were uniform across the greenhouse. A significant effect due to soils indicated that differences in yield occurred between soils averaged over all levels of sulfur. In Table 13 plant yields are shown for those soils on which a significant response was obtained from the applied sulfur.

Table 12. Analysis of variance of dry matter yields of ryegrass at harvest 1, of Experiment 1/68

Source of variation	df	Mean square	F
Blocks	2	0.0440	0.394
Soils	20	7.9218	70.803**
Error (a)	40	0.1119	
Sulfur	4	1.2046	32.498**
Soil x sulfur	80	0.0526	1.419
Error (b)	168	0.0370	
Total	314		

These data show that the yield differences between soils were related to factors other than sulfur.

Because this experiment had been planned to maintain the nutrient supply other than sulfur uniform between soils by regular application of Hoagland's S-free nutrient solution to the sand layer below the test soil, differences between soils of this magnitude were not envisaged. It was known, however, that considerable differences in the available N, P and K contents existed in the soils prior to potting (Table 38, Appendix). Graphs made of ryegrass yields from the 30 ppm S treatment versus available N, P

Table 13. Response of ryegrass to applied sulfur, at harvest 1, of Experiment 1/68[a]

Soil	Yield of dry matter (g/pot) S added (ppm) 0	7.5	15	22.5	30	Av.	Percent S in ryegrass, no S applied
Hamburg	1.41	2.25	2.56	2.50	2.32	2.21	.147
Hagener	1.59	2.37	2.08	2.08	2.18	2.06	.163
Webster	2.96	3.33	3.43	3.44	3.43	3.32	.144
Sharpsburg	3.28	3.70	3.87	3.78	3.86	3.70	.177
Fayette	2.98	3.32	3.34	3.22	3.39	3.25	.189
Clarion	2.69	2.94	3.06	2.97	3.20	2.97	.192
Tama	2.77	3.13	3.19	3.09	3.32	3.10	.286
Marshall	3.63	4.04	3.93	4.07	4.03	3.95	.253
Albaton	3.25	3.67	3.80	3.43	3.76	3.59	.304
Weller	4.93	5.03	5.28	5.23	5.18	5.13	.300
Av.	2.89	3.14	3.21	3.19	3.23		

[a]LSD 5%, differences between two soil means, 0.25; differences between two sulfur means, 0.07; differences between two levels of sulfur on the same soil, 0.31; differences between two soils at the same or different sulfur level, 0.37.

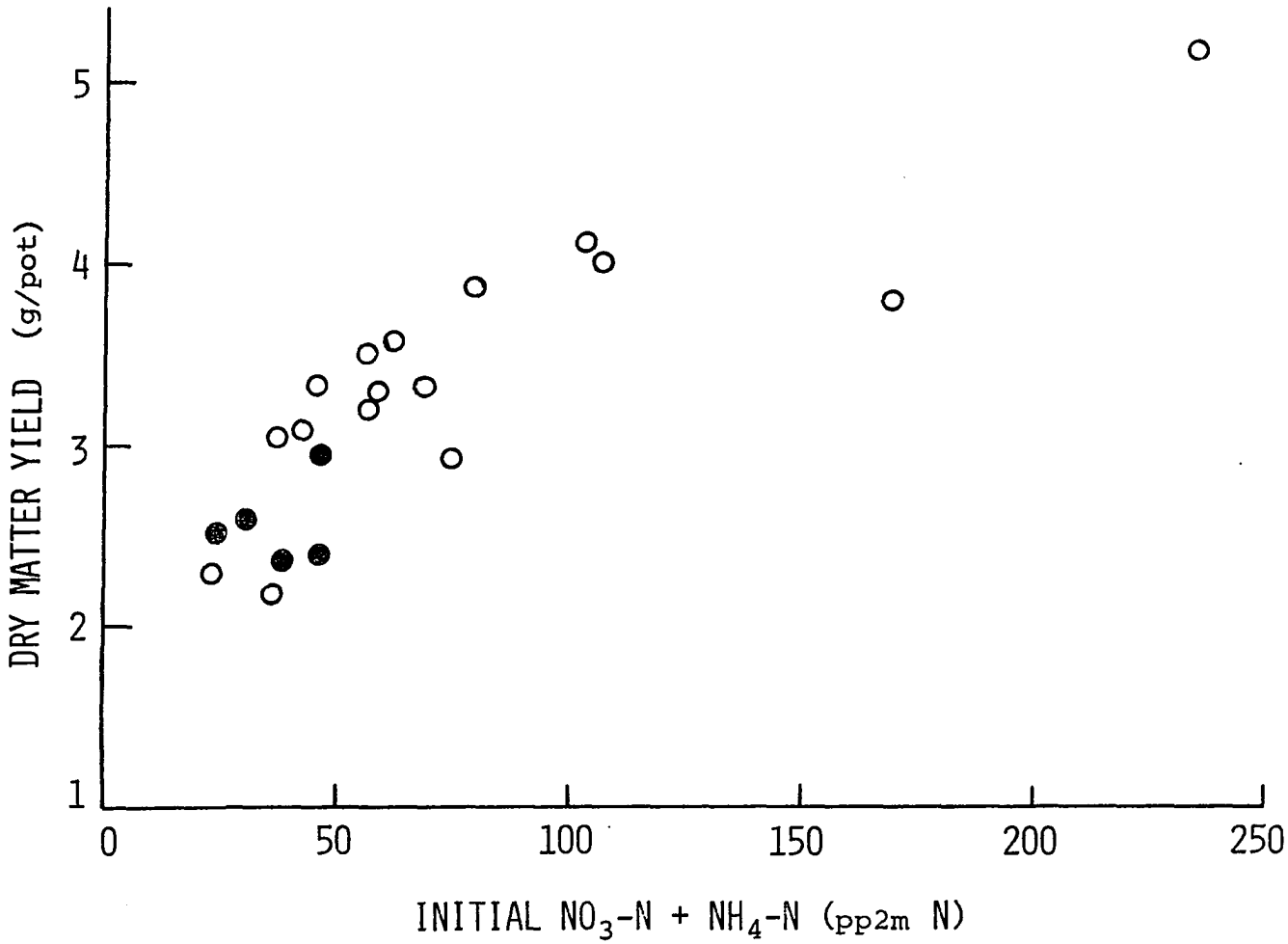
and K suggested that available N in the soil prior to potting was related to yield differences between soils at harvest 1 (Figure 10). The relationship between available N, P and K and ryegrass yield from the 30 ppm S treatment was examined by multiple regression techniques. The relationship obtained between initial fertility and ryegrass yield at the first harvest is given by the equation

$$Y = 2.51 + .013X_1 + .008X_2 + .0003X_3$$

where Y = predicted dry matter yield of ryegrass (g/pot); X_1 = NO_3-N + NH_4-N in the soil at potting (pp2m); X_2 = available P (pp2m); and X_3 = exchangeable K (pp2m). A "t" test of the regression coefficients showed that only the regression coefficient for available nitrogen was significant ($t = 6.5$ and tabulated $t_{(.05)} = 2.11$ for 17 df).

The explanation for dry matter yield differences between soils in the first harvest, is thought due to differences in fertility, mainly nitrogen. Although more than sufficient NPK and other nutrients were applied to the sand layer below the soil in all greenhouse pots at the time of transfer, these nutrients would not be accessible to the ryegrass plants until the roots had grown through the soil and made contact with the sand. Therefore, ryegrass that was transferred to soils of high fertility would have a considerable initial advantage over

Figure 10. Relationship between ryegrass yield supplied with 30 ppm S at harvest 1 and available N, initially present in the soils

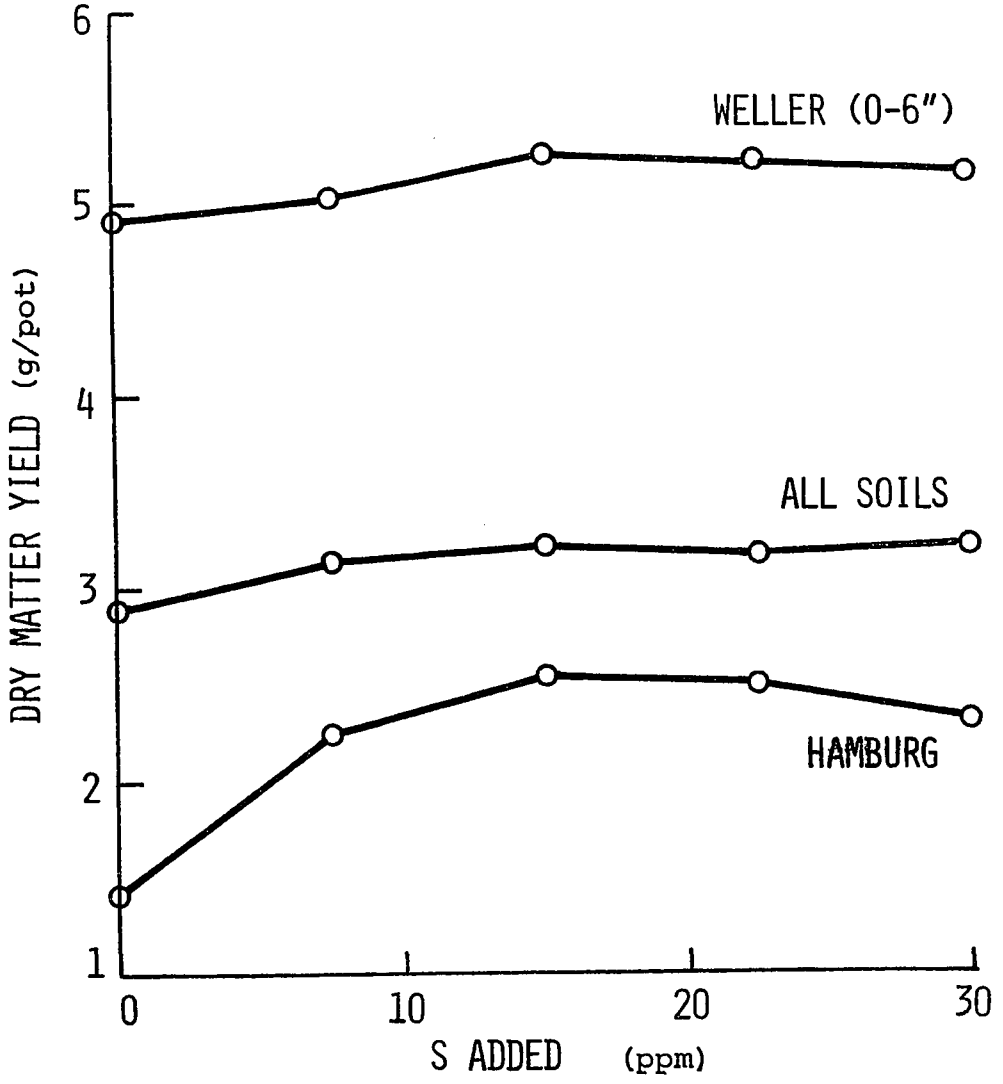

DRY MATTER YIELD (g/pot)
5
4
3
2
1
0
50
100
150
200
250
INITIAL NO_3-N + NH_4-N (pp2m N)

those plants that were transferred to a soil of low inherent fertility. Moreover, roots growing into soils of high fertility would tend to grow more rapidly, and hence would probably reach the main nutrient supply in the sand layer before those roots in the low fertility soil. Observations made on root growth indicated that at least seven days were required for roots to grow through the soil layer to the sand below. Differences in the nutrient supply, available to the ryegrass roots at transfer is considered to be the main factor causing soil to soil differences in yield at the first harvest.

Over all soils the effect of sulfur treatment on yield was highly significant (Table 12). The effect of sulfur on dry matter yield was curvilinear and is shown for the average of all soils and the range in Figure 11. Ten of the 16 surface soils in the experiment gave a response to the 7.5 or 15 ppm level of added sulfur that was significant at the 5 percent level. These responses are shown in Table 13. Above 15 ppm of added sulfur, yields remained fairly constant. On the Hamburg soil the decline in yield between the 15 and 30 ppm S level was not significant.

Of the soils that were sulfur responsive at first harvest, six of the ten produced ryegrass which, in the absence of applied sulfur, contained less than 0.25 percent S, the critical level for sulfur in ryegrass (McNaught and

Figure 11. Effect of applied sulfur on dry matter yields, at harvest 1, for all soils and for the range


6
5
4
3
2
1
DRY MATTER YIELD (g/pot)
WELLER (0-6")
ALL SOILS
HAMBURG
0
10
20
30
S ADDED (ppm)

Christoffels, 1961). None of the subsoils responded to sulfur and the sulfur content of the untreated ryegrass on all of these soils exceeded 0.31 percent. Neither of the out-of-state soils, Thurman sand and Dorset sandy loam, gave significant responses to applied sulfur.

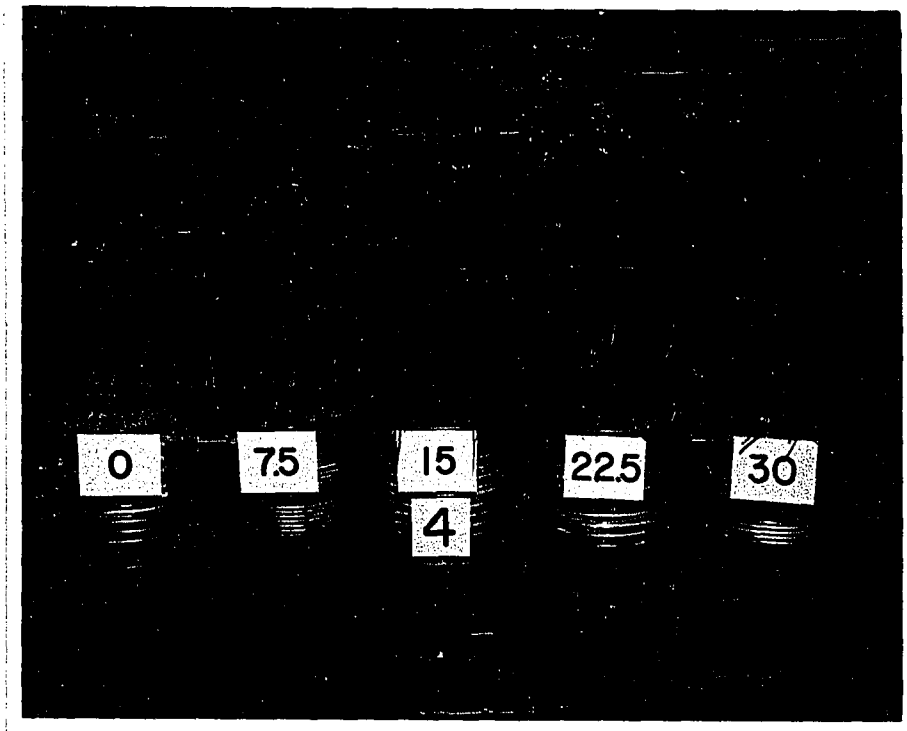
The soils by sulfur interaction was nonsignificant indicating that, overall, the dry matter response to sulfur was similar from soil to soil.

After harvest 1, the ryegrass plants on all soils, with the exception of the Monona and Albaton surface soils and the Weller subsoil, showed marked responses to applied sulfur. A typical response is that shown in Figure 12 for the Hamburg soil. The zero sulfur treatment and the 30 ppm S treatment for the Hamburg soil are also shown in Figure 13. Typical symptoms of sulfur deficiency are apparent, with thin, rather erect pale yellowish-green leaves, with the chlorosis being fairly uniformly spread over the whole leaf surface. There was considerable death of older leaves and firing of the distal portion of newly-matured leaves.

The analysis of variance for the dry matter yields from all five harvests of the experiment is given in Table 14. Differences in dry matter yields between blocks were highly significant. Ryegrass from Block 2 (center bench) yielded an average of 0.14 g more than the grass from

Figure 12. Response of ryegrass to applied sulfur on Hamburg silt loam prior to harvest 3. (Dry matter yields at harvest were 0.28, 1.12, 2.28, 4.12 and 4.38 g per pot for 0, 7.5, 15, 22.5 and 30 ppm S respectively)

Figure 13. Severe sulfur deficiency in ryegrass at left compared with normal growth at right, in Hamburg silt loam prior to harvest 3


0
7.5
15
4
22.5
30

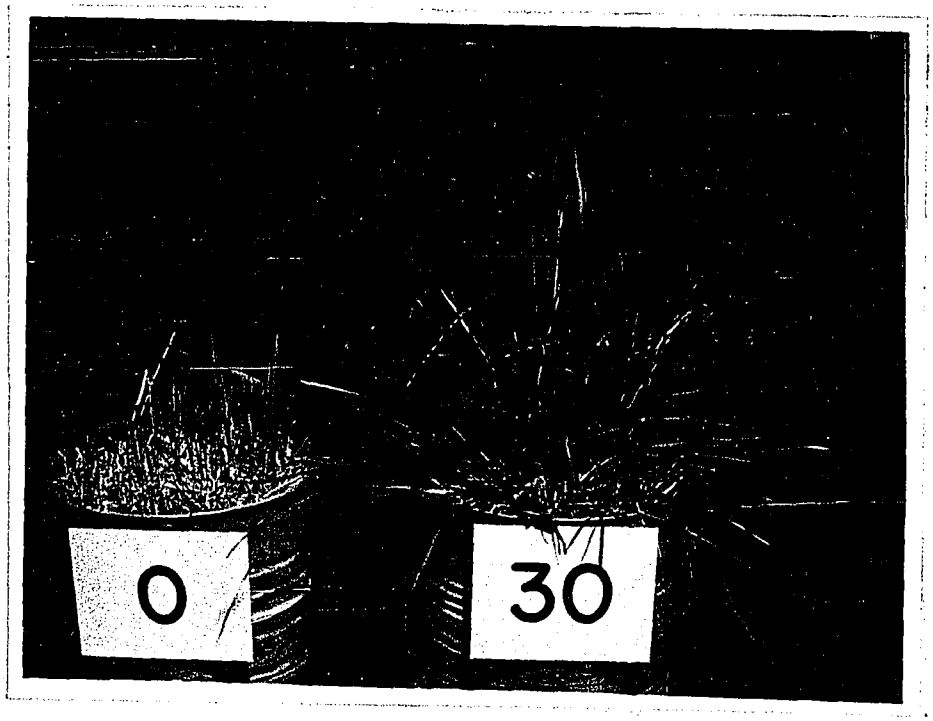

0
30

Table 14. Analysis of variance of dry matter yields over five harvests, on Experiment 1/68

Source of variation	df	Mean square	F
Blocks	2	4.1271	23.59**
Soils	20	28.7948	164.56**
Error (a)	40	0.1750	
Sulfur	4	157.3853	1691.24**
Soil x sulfur	80	0.5405	5.81**
Error (b)	168	0.0931	
Harvests	4	191.4514	1985.79**
Soil x harvest	80	3.1957	33.15**
Sulfur x harvest	16	16.5835	172.01**
Soil x sulfur x harvest	320	0.3885	4.03**
Error (c)	840	0.0964	
Total	1575		

either of the outside blocks. While blocks differences were not apparent in the first harvest they developed as the drop in temperature outside the greenhouse created temperature gradients from the center to the sides of the greenhouse. A temperature difference of merely a few degrees would be sufficient to account for an average yield

differences of 0.14 g/pot between blocks (Mitchell, 1956).

Soil to soil differences in dry matter yields over five harvests were large and highly significant (Table 43 of the Appendix). These differences resulted mainly from differences in sulfur supplying capacity of the soils, as will be shown later, and, to a lesser extent from initial differences in fertility. The effect of sulfur on yield over all harvests and soils was highly significant, and is shown in Figure 14 to be linear (the linear regression accounted for 99 percent of the variance due to sulfur). The effect of sulfur on the total yield of ryegrass on both the highest and lowest yielding soils, Monona (0-6 in) and Webster (18-24 in) is also essentially linear. A significant soils by sulfur interaction indicates that sulfur had not given a response of the same magnitude on all soils. This is apparent in Table 43, of the Appendix, which shows the response to sulfur on each of the soils over all five harvests. Thus a soil such as Weller (18-24 in), which has a relatively high sulfur supplying capacity gave a very small response to applied sulfur compared with Hamburg, which had a very low sulfur supplying capacity.

The nature of this soil by sulfur interaction is further illustrated in Figure 15 which indicates three quite distinct response patterns to applied sulfur. The first response shown, Figure 15a, was typical for most of

Figure 14. Effect of applied sulfur on dry matter yield for harvests 1-5 for all soils and for the range

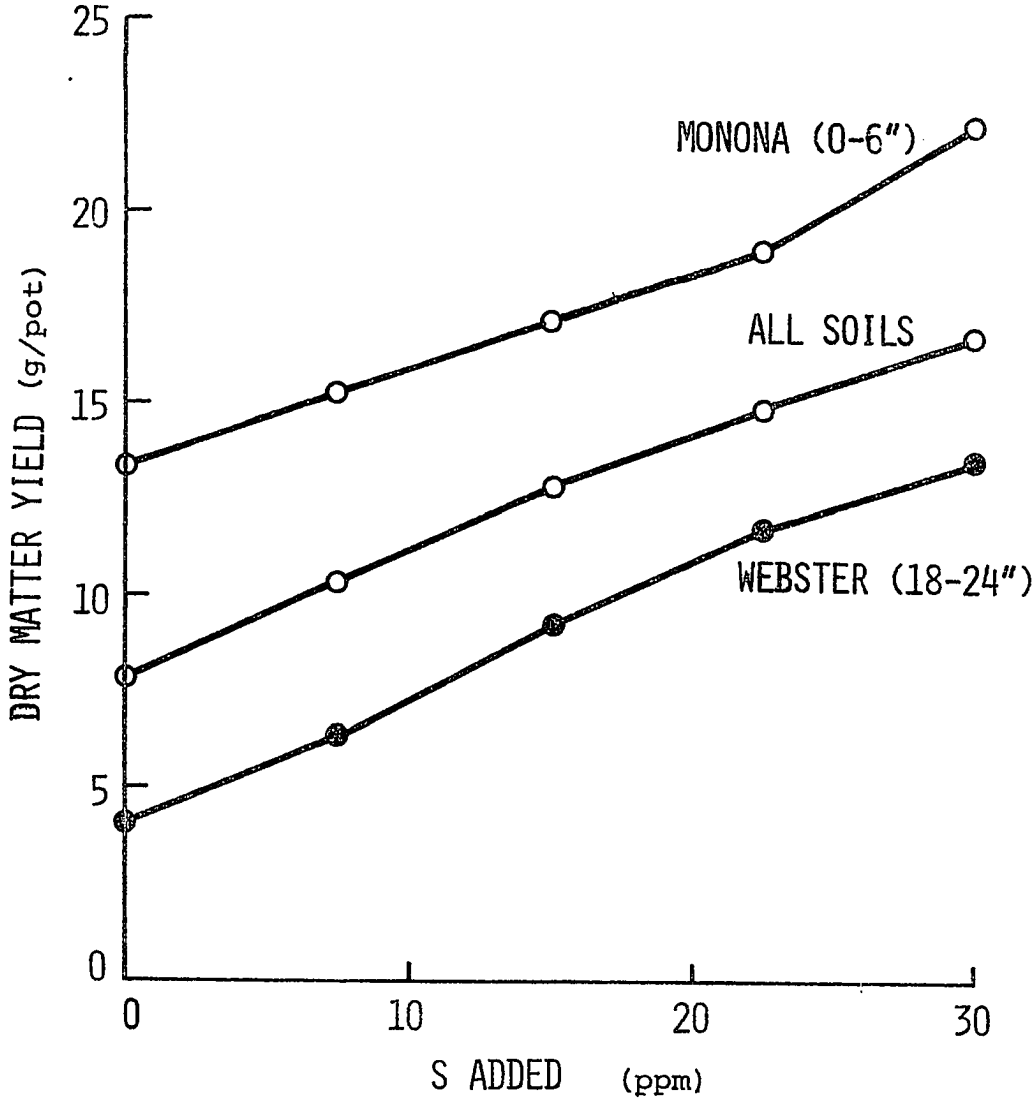
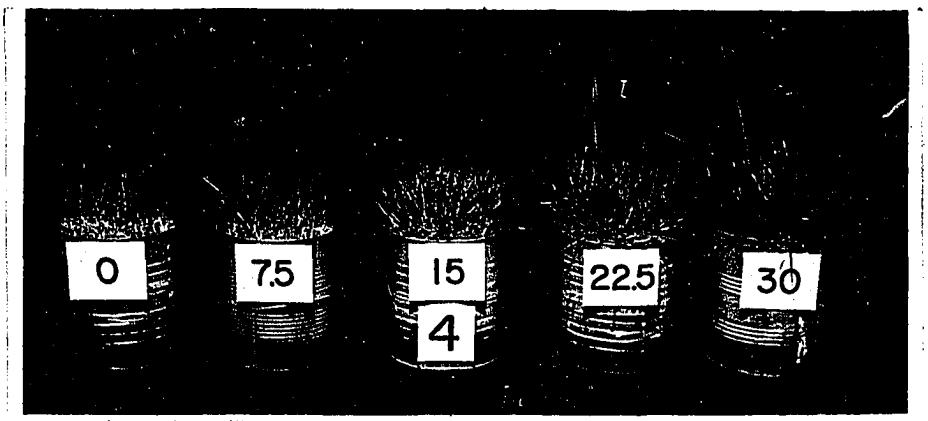

25
20
15
10
5
0
DRY MATTER YIELD (g/pot)
MONONA (0-6")
ALL SOILS
WEBSTER (18-24")
0
10
20
30
S ADDED (ppm)

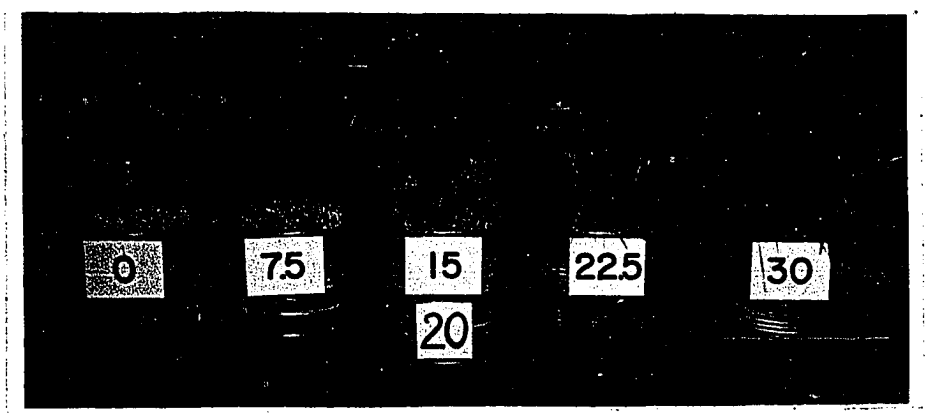
Figure 15. Effect of applied sulfur on ryegrass growth, prior to harvest 4, in Experiment 1/68 showing three types of response

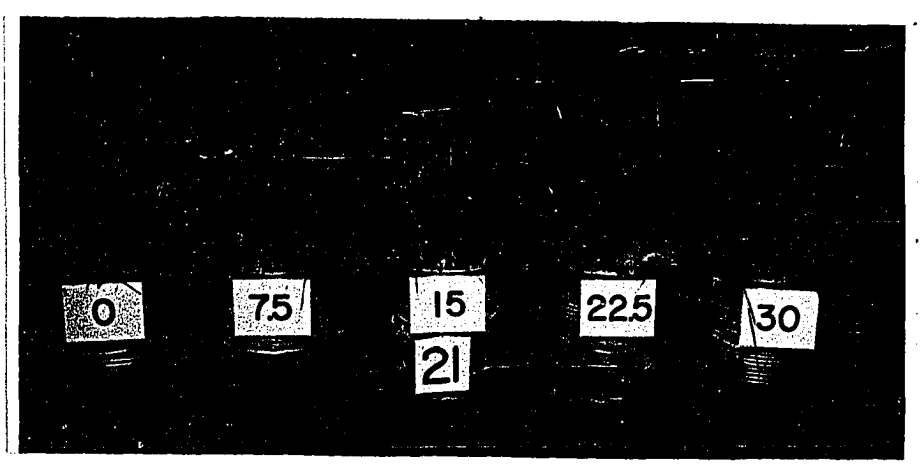
Figure 15a. Response to sulfur on a sulfur deficient surface soil, Hamburg silt loam

Figure 15b. Response to sulfur on a sulfur deficient subsoil, Fayette silt loam (18-24 in)

Figure 15c. Response to sulfur on a sulfur sufficient subsoil, Weller silt loam (18-24 in)


0
7.5
15
4
22.5
30


0
75
15
20
225
30


0
75
15
21
225
30

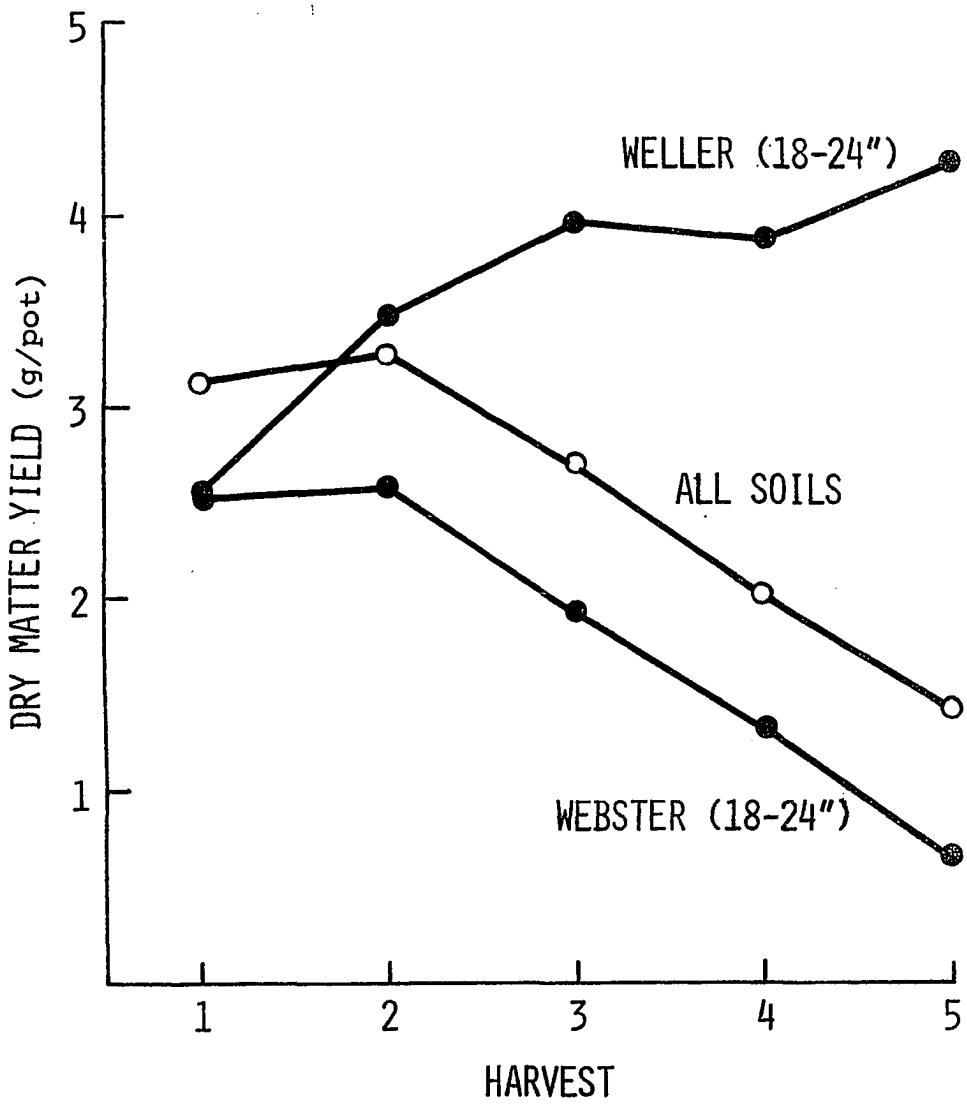
the surface soils with sulfur becoming progressively limiting with each harvest. As sulfur was exhausted at a given level of applied sulfur, dry matter yields fell to a level similar to that of the control treatment. On these surface soils, apparently, slow mineralization of sulfur resulted in a continuous though very slow growth of ryegrass plants.

The second type of response illustrated (Figure 15b), is typical for four of the subsoils in this study. Initially the response was identical to that of the surface soils, but as ryegrass progressively removed both the available soil sulfur initially present, plus applied sulfur, plants became severely sulfur deficient. Growth then ceased almost completely and many plants died, so acute was the deficiency of sulfur. Death of practically all plants occurred on both the Webster and Fayette subsoils.

The third type of response occurred on the Weller subsoil and is illustrated in Figure 15c. After three harvests growth was uniformly vigorous at all levels of applied sulfur. A response of this type clearly indicates that the soil was well supplied with available sulfur.

Ryegrass yields over all soils were highest at the second harvest and thereafter declined linearly, as sulfur became progressively more limiting. The average and the range for all soils is shown in Figure 16. Yields from

Figure 16. Effect of harvest on dry matter yield for all soils, and for the range of soils, averaged over all levels of applied sulfur


5
4
3
2
1
DRY MATTER YIELD (g/pot)
WELLER (18-24")
ALL SOILS
WEBSTER (18-24")
1
2
3
4
5
HARVEST

most soils followed the trend indicated for the average of all soils, but yields from the Weller subsoil tended to increase with successive harvests. Other soils not following the trend and thus contributing to the significant soil by harvest interaction were the Monona and Albaton surface soils.

The highly significant sulfur by harvest interaction is illustrated in Figure 17, whereby the response of ryegrass to sulfur over all soils changes with successive harvests. In the first two harvests yield of dry matter increased at a decreasing rate as the amount of added sulfur was increased. In the third harvest the increase in yield was almost linear with the amount of sulfur added, while in harvests four and five the increase in dry matter increased at an increasing rate as the amount of added sulfur increased. When the cumulative dry matter yields are plotted for the average of all soils, as in Figure 18, the cumulative response to applied sulfur can be seen at any given harvest. The cumulative response is shown to change, from virtually no response at harvest one to a curvilinear response at harvests two and three, and to a linear response at harvests four and five.

Percent S in ryegrass

Percent sulfur in ryegrass is shown for the whole experiment in Table 42, of the Appendix. An analysis of variance on the first harvest data, Table 15, shows that

Figure 17. Effect of sulfur on dry matter yield, for five successive harvests, averaged over all soils

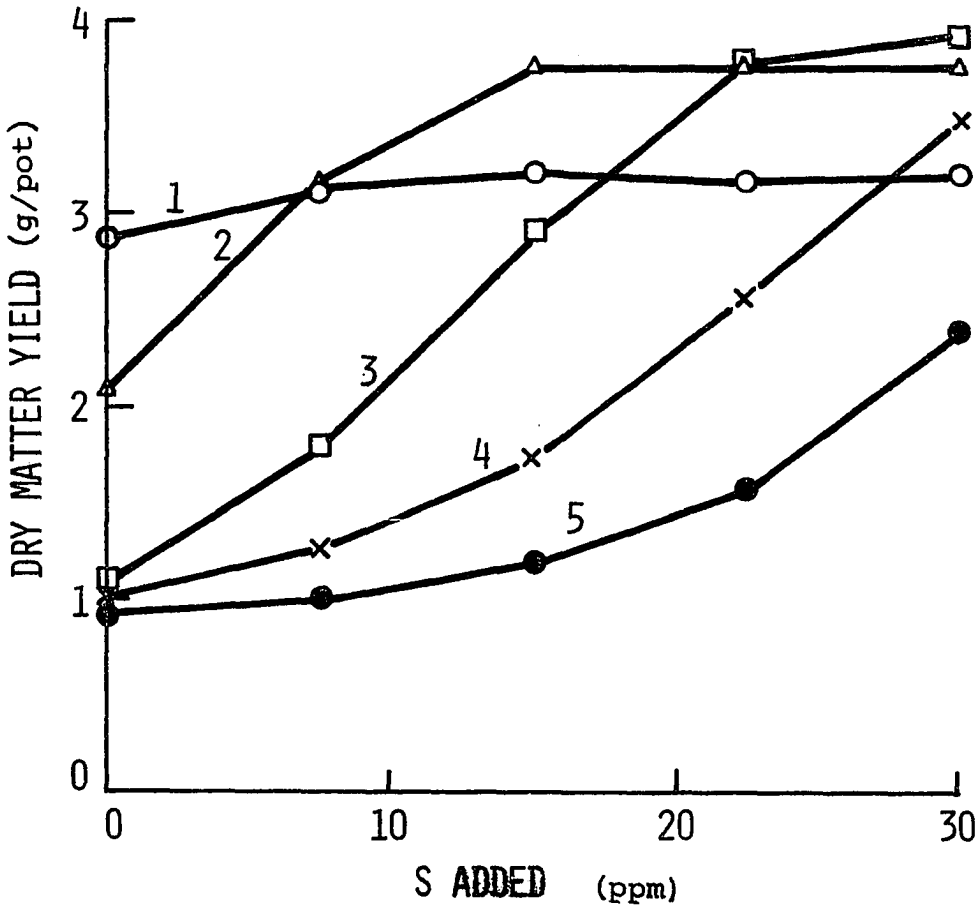

DRY MATTER YIELD (g/pot)
4
3
2
1
0
1
2
3
4
5
0
10
20
30
S ADDED (ppm)

Figure 18. Cumulative response of ryegrass to applied sulfur over five harvests, averaged over all soils

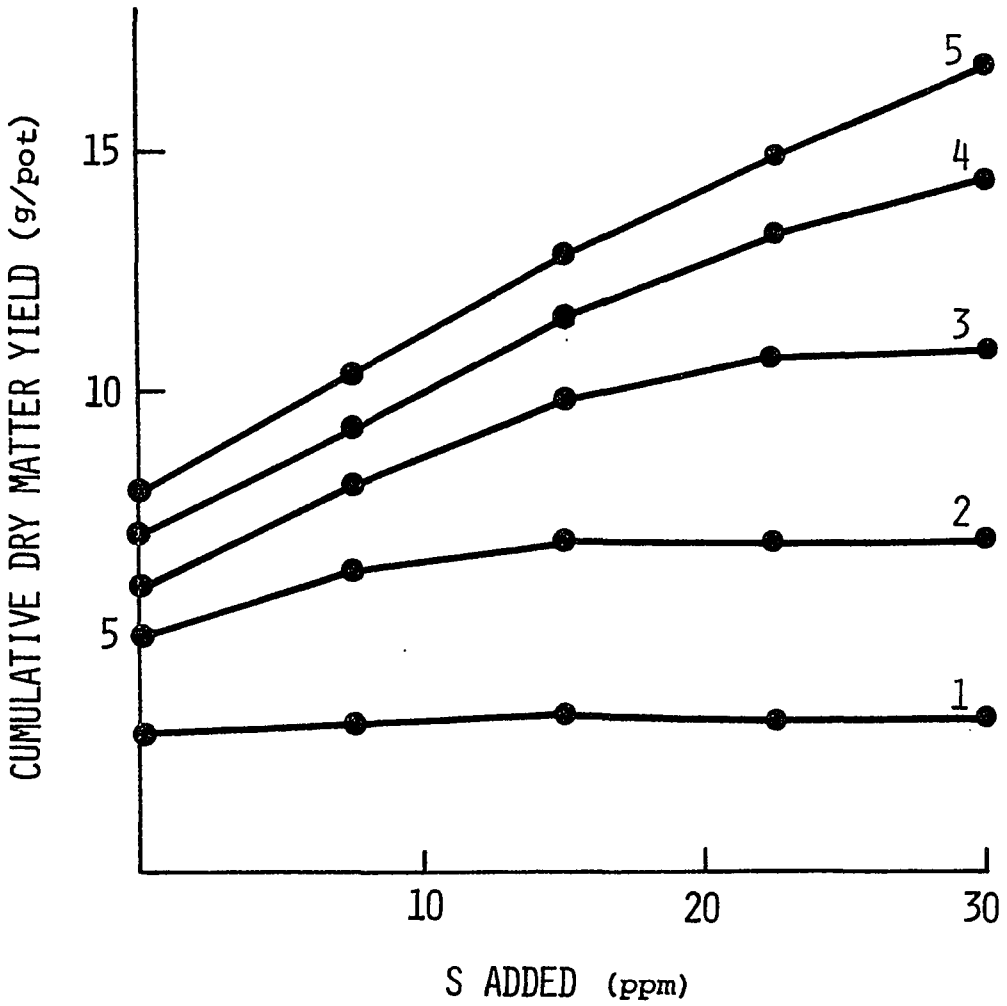

CUMULATIVE DRY MATTER YIELD (g/pot)
15
10
5
10
20
30
S ADDED (ppm)
5
4
3
2
1

Table 15. Analysis of variance of percent S in ryegrass for harvest 1, of Experiment 1/68

Source of variation	df	Mean square	F
Blocks	2	0.0004	0.28
Soils	20	0.0429	27.79**
Error (a)	40	0.0015	
Sulfur	4	0.6213	572.76**
Soil x sulfur	80	0.0070	6.48**
Error (b)	168	0.0011	
Total	314		

the effects of soils and of sulfur application were highly significant. In the absence of applied sulfur, there were large differences in percent S in ryegrass between soils which were found to be significantly correlated with sulfate sulfur extracted by 0.1 M LiCl. Percent S in the control treatments for harvest 1 averaged 0.28 percent over all soils and ranged from 0.14 percent S in Webster clay loam to 0.50 percent S in both Monona silt loam and the Weller silt loam subsoil. In six of the surface soils the sulfur content of ryegrass was less than 0.25 percent which has been considered by McNaught and Christoffels (1961) to be

the critical level for total S in ryegrass leaves. Yields of ryegrass were increased significantly on these soils from applications of as little as 7.5 ppm sulfur.

The response in percent sulfur to sulfur applied was highly significant and curvilinear for harvest 1. This response is shown in Figure 19a for the average of all soils and the range. The rate of increase of percent S in ryegrass decreased as the rate of application of S increased. There would appear to be a "threshold" level of percent S in ryegrass of about 0.60 percent, above which percent S changed very little with added sulfur; neither Monona (0-6 in) nor Weller subsoil, each with 0.50 percent S in the control treatment gained more than 0.10 percent S from an application of 30 ppm S, whereas, in the S deficient Webster soil an application of 15 ppm S, as gypsum, increased the sulfur content from 0.14 to 0.39 percent S. This is the basis of the highly significant soil by sulfur interaction.

The analysis of variance for the complete experiment is shown in Table 16. The main effects of soils, sulfur treatment and harvests were all highly significant. The effect of harvest was large. Figure 19 shows how the sulfur content dropped sharply as successive harvests depleted both applied and native sulfur. The soil by sulfur interaction was highly significant but its magnitude declined in later harvests compared with that in the first harvest

Figure 19. Effect of applied sulfur on the percent sulfur in ryegrass in harvest 1, harvest 3 and harvest 5 for the average of all soils and the range, (Monona (6) and Webster (2))

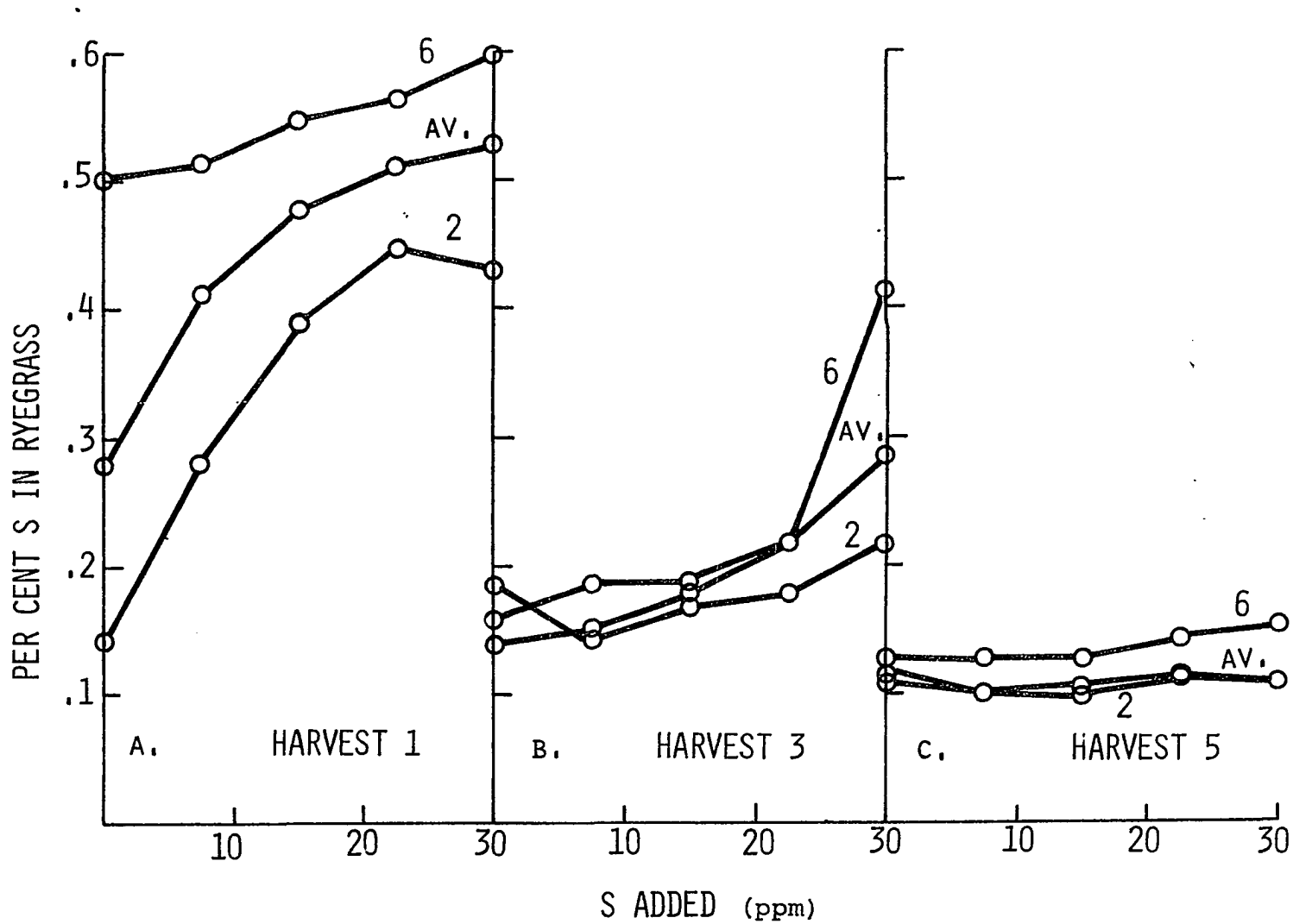

PER CENT S IN RYEGRASS
.6
.5
.4
.3
.2
.1
6
AV.
2
A. HARVEST 1
B. HARVEST 3
C. HARVEST 5
10
20
30
S ADDED (ppm)

Table 16. Analysis of variance of percent sulfur in ryegrass for five harvests, in Experiment 1/68

Source of variation	df	Mean square	F
Blocks	2	0.0029	1.43
Soils	20	0.0425	20.91**
Error (a)	40	0.0020	
Sulfur	4	0.9162	739.43**
Soil x sulfur	80	0.0039	3.04**
Error (b)	168	0.0012	
Harvests	4	5.3009	5063.11**
Soil x harvest	80	0.0146	13.93**
Sulfur x harvest	16	0.1741	166.31**
Soil x sulfur x harvest	320	0.0047	4.44**
Error (c)	840	0.0010	
Total	1574		

(F values for the soil by sulfur interaction were 6.5, 4.3 and 3.0 for harvest 1, harvests 1-3 and harvests 1-5 respectively). In Figure 19 sulfur levels in the ryegrass are shown to decline toward a minimum value with successive harvests. Therefore, with harvest, the effect of sulfur level on the S content of ryegrass tends to become very

similar from soil to soil.

Yield of sulfur

The mean yields of sulfur in ryegrass for all rates of added sulfur, soils and harvests are given in Table 42 of the Appendix. In Tables 17 and 18, the yields of sulfur summed over five harvests are given; yields of sulfur in Table 17 include the contribution from the silica sand whereas yields in Table 18 do not.

A useful index of plant available sulfur is the yield of sulfur in plants grown on soils to which no sulfur has been applied. In Figure 20 cumulative values of sulfur uptake over five harvests not adjusted for the sulfur contribution from silica sand have been plotted in order, from lowest to highest. These sulfur yields show a tenfold range of uptake varying from 3.8 mg S/pot (2.5 mg S/kg soil) on Hamburg silt loam, to 41 mg S/pot (27 mg S/kg soil) on the subsoil of Weller silt loam. The mean uptake in the untreated ryegrass, including the sulfur from silica sand, was 15.6 mg S/pot (10.4 mg S/kg soil). Sulfur was not taken up in equal increments over all harvests. In the untreated surface soils an average of 72 percent of the total uptake was removed in the first two harvests. In the subsoils however, with the exclusion of the atypical Weller, an average of 93 percent of the total uptake occurred in the first two harvests. This difference

Table 17. Effect of applied sulfur on yield of sulfur in ryegrass, on 21 soils, summed over five harvests (yields include sulfur supplied by silica sand)

Soil	Yield of sulfur (mg/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Surface soils			
Hamburg	3.75	14.91	22.73	33.52	37.96	22.58
Hagener	5.71	14.57	22.15	32.27	41.25	23.19
Webster	10.48	17.30	29.55	39.56	42.19	27.80
Thurman	11.77	20.16	28.88	35.22	45.68	28.34
Dorset	11.79	20.48	32.66	41.87	50.19	31.40
Sharpsburg	10.75	21.83	30.69	40.53	51.54	30.80
Fayette	11.34	20.28	31.71	42.87	52.49	31.74
Clarion	12.43	20.19	29.80	40.02	51.10	30.71
Tama	12.86	23.28	30.07	41.59	56.25	32.82
Sarpy	14.63	28.52	34.55	46.72	49.89	34.86
Marshall	13.91	24.65	31.85	42.34	53.49	33.25
Grundy	18.13	26.35	39.34	48.02	55.55	37.48
Albaton	20.75	36.32	50.35	57.70	68.04	46.63
Ida	21.21	28.15	44.66	52.35	54.74	40.24
Weller	24.30	35.91	42.97	58.26	56.86	43.67
Monona	37.86	42.28	48.43	55.71	72.43	51.32

Table 17. (Continued)

Soil	Yield of sulfur (mg/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Subsoils			
Clarion	7.95	18.25	28.38	37.94	42.29	26.95
Webster	9.38	14.87	22.95	38.89	44.58	26.13
Fayette	10.75	21.76	30.90	33.81	45.44	28.53
Monona	16.30	26.90	37.20	46.35	53.85	36.10
Weller	41.50	44.95	52.51	57.18	57.33	50.70

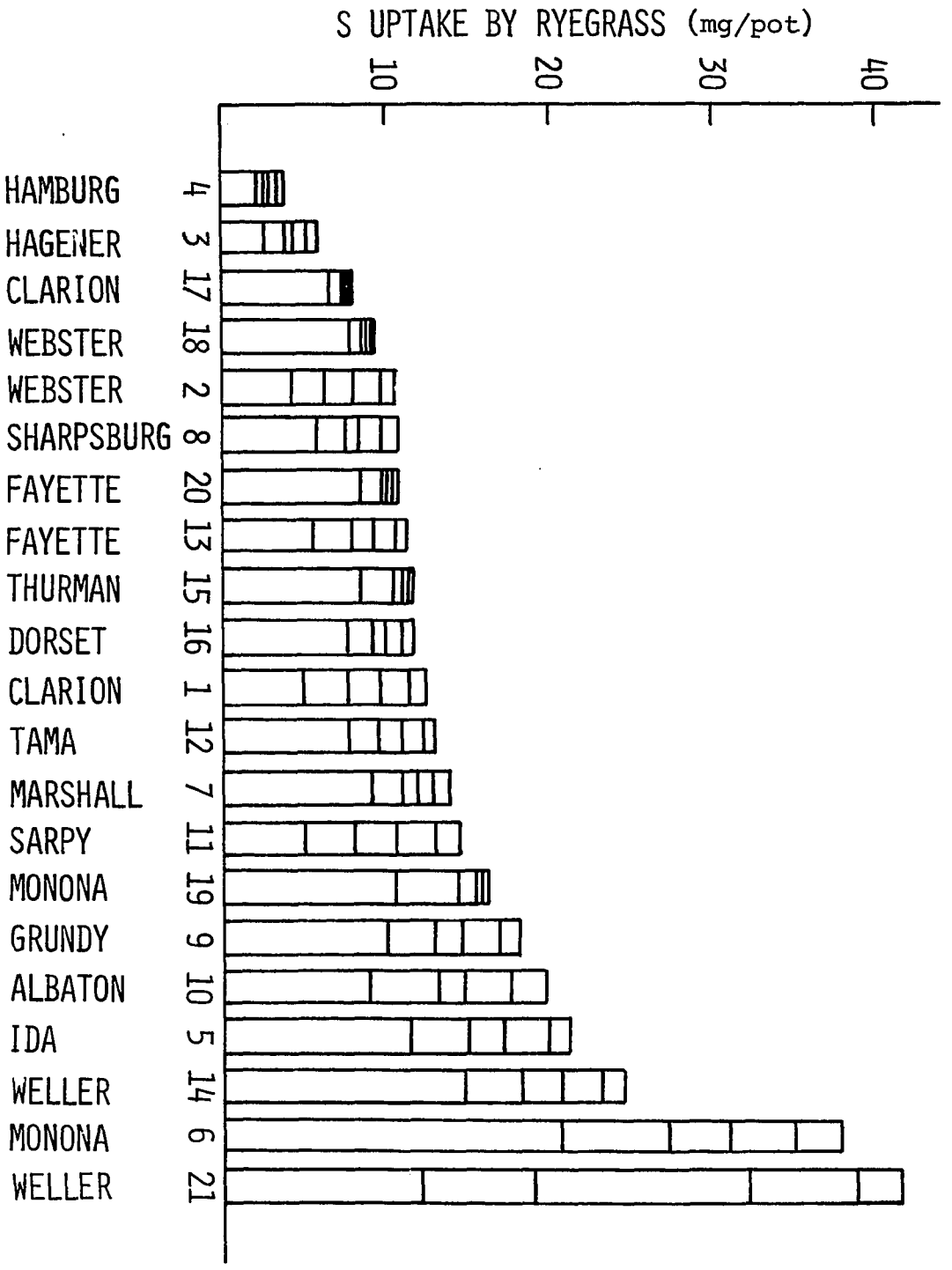
Table 18. Effect of applied sulfur on yield of sulfur in ryegrass, on 21 soils, summed over five harvests (yields adjusted for sulfur supplied by silica sand)

Soil	Yield of sulfur (mg/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Surface soils			
Hamburg	1.07	12.23	20.05	30.84	34.28	19.90
Hagener	1.93	10.79	18.37	28.49	37.78	19.41
Webster	7.80	14.62	26.87	36.88	39.51	25.12
Thurman	7.99	16.38	25.10	31.44	41.90	24.56
Dorset	8.01	16.70	28.88	38.09	46.41	27.62
Sharpsburg	8.07	19.15	28.01	37.85	48.86	28.12
Fayette	8.66	17.60	29.03	40.19	49.81	29.06
Clarion	9.75	17.51	27.12	37.34	48.42	28.03
Tama	10.18	20.60	27.39	38.91	53.57	30.14
Sarpy	10.85	24.74	30.77	42.94	46.11	30.08
Marshall	11.23	21.97	29.17	39.66	50.81	30.57
Grundy	14.45	23.67	36.66	45.34	52.87	34.80
Albaton	18.07	33.64	47.67	55.02	65.36	43.95
Ida	18.53	25.47	41.98	49.67	51.06	37.56
Weller	21.62	32.23	40.29	55.58	54.18	40.99
Monona	35.18	39.60	45.75	53.03	69.75	48.64

Table 18. (Continued)

Soil	Yield of sulfur (mg/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Subsoils			
Clarion	5.27	15.57	25.70	35.26	39.61	24.27
Webster	6.70	12.19	20.27	36.21	41.90	23.45
Fayette	8.07	19.08	28.22	31.13	42.76	25.85
Monona	13.62	23.22	34.52	43.67	50.17	33.42
Weller	38.82	42.27	49.83	54.50	54.65	48.02

Figure 20. Cumulative uptake of sulfur by ryegrass, in the five harvests, from different soils where no sulfur was added (uptake unadjusted for silica sand sulfur)


S UPTAKE BY RYEGRASS (mg/pot)
10
20
30
40
HAMBURG 4
HAGENER 3
CLARION 17
WEBSTER 18
WEBSTER 2
SHARPSBURG 8
FAYETTE 20
FAYETTE 13
THURMAN 15
DORSET 16
CLARION 1
TAMA 12
MARSHALL 7
SARPY 11
MONONA 19
GRUNDY 9
ALBATON 10
IDA 5
WELLER 14
MONONA 6
WELLER 21

between surface soils and subsoils suggests a greater availability of the subsoil sulfur. It could result however, from a rapid depletion of water soluble sulfate in both surface soils and subsoils, followed by a slow release of available sulfate from mineralization or other mechanisms in surface soils, and virtually no release at all from mineralization in subsoils.

An analysis of variance for the complete experiment is shown in Table 19. The main effects of soils, sulfur treatment and harvests and all of the interactions were highly significant. The responses of sulfur yield in ryegrass to applied sulfur for harvests 1, harvests 1-3 and harvests 1-5 are shown in Figure 21 for the average of all soils and for the lowest and highest yielding surface soils, Hamburg and Monona. In the first harvest the response was curvilinear with the rate of increase in uptake of sulfur decreasing as the amount of sulfur added was increased. With successive harvests, the response to sulfur changed to a linear function of sulfur added (r^2 for the linear effect of sulfur in harvests 1-5 was 0.98). In harvests 1-3 the effect of sulfur over all soils was linear.

A major part of the sulfur applied to each soil was recovered in five harvests. In the calculation of recovery of applied sulfur an assumption was made, that at any level of applied sulfur on a given soil, that part of the sulfur

Table 19. Analysis of variance for yields of sulfur in ryegrass for five harvests, in Experiment 1/68

Source of variation	df	Mean square	F
Blocks	2	3.5306	2.41
Soils	20	206.5684	140.96**
Error (a)	40	1.4654	
Sulfur	4	2612.5527	1592.49**
Soil x sulfur	80	5.5812	3.40**
Error (b)	168	1.6405	
Harvest	4	7534.1641	4992.36**
Soil x harvest	80	42.5381	28.19**
Sulfur x harvest	16	204.0570	135.21**
Soil x sulfur x harvest	320	5.6464	3.74**
Error (c)	840	1.5091	
Total	1574		

in the plant which came from the soil, would be equal to the sulfur taken up from soils to which no sulfur was added. The percent recovery of applied sulfur given in Table 20 shows that over all levels of S applied, values range from 40 percent on the Weller subsoil to 122 percent on the Albaton surface soil. Laboratory error leading to low values for the no sulfur treatment on the Albaton soil,

Figure 21. Effect of applied sulfur, on sulfur uptake in ryegrass for harvest 1, harvests 1-3 and harvests 1-5 for the average of all soils, for the lowest yielding surface soil, Hamburg (4) and for the highest yielding surface soil, Monona (6)

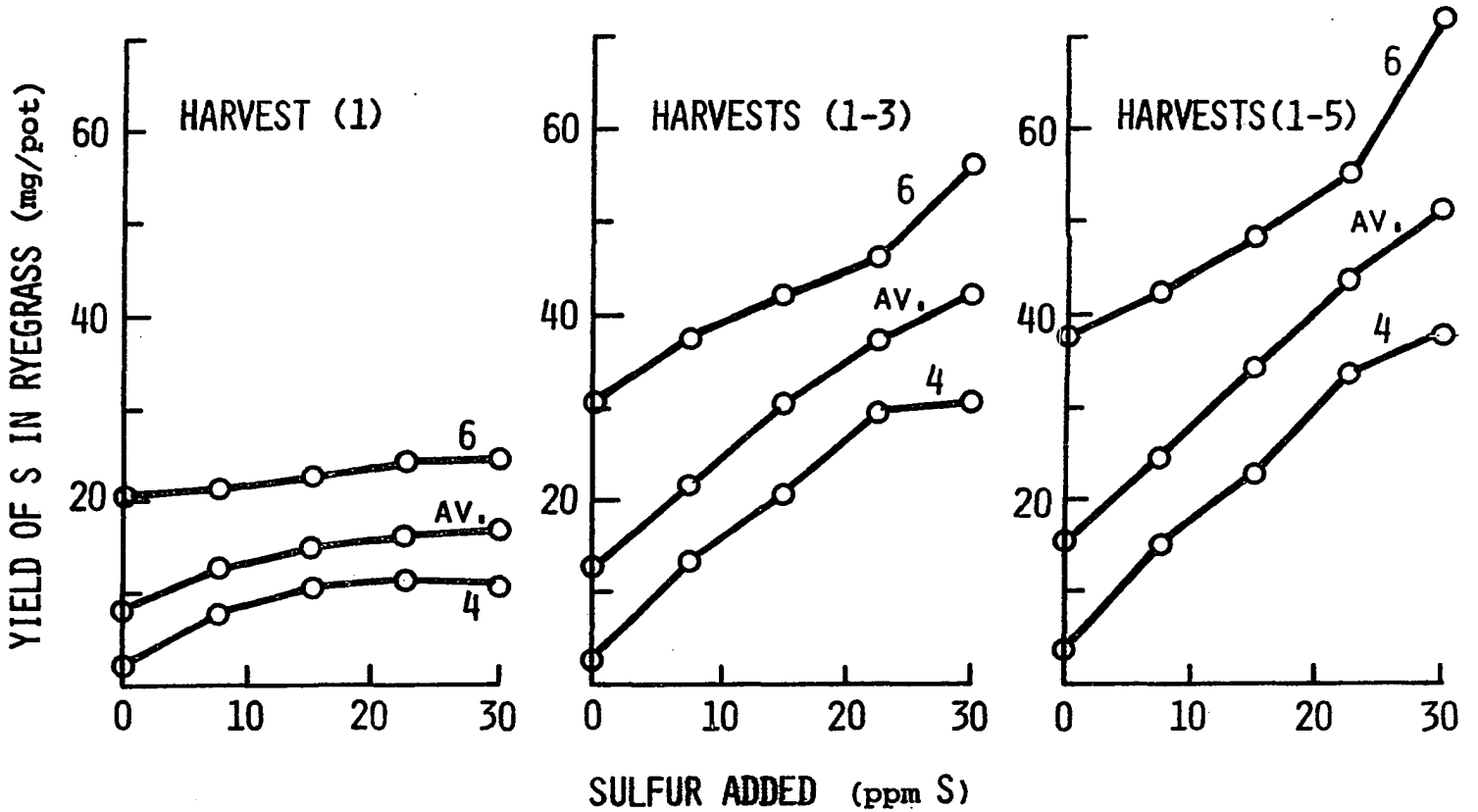

HARVEST (1)
HARVESTS (1-3)
HARVESTS(1-5)
YIELD OF S IN RYEGRASS (mg/pot)
SULFUR ADDED (ppm S)
6
AV.
4
0
10
20
30
40
60

Table 20. Recovery of added sulfur in ryegrass, from 21 soils, over five harvests

Soil	Percent recovery of added S ppm S added					Percent recovery from regression mean
	7.5	15	22.5	30	Mean	
			Surface soils			
Hamburg	99	84	88	74	86	77 ± 7
Hagener	79	73	79	80	78	79 ± 6
Webster	61	85	86	71	76	76 ± 12
Thurman	75	76	70	75	74	74 ± 10
Dorset	77	93	89	85	86	87 ± 8
Sharpsburg	99	89	88	91	91	87 ± 4
Fayette	80	91	93	91	89	93 ± 6
Clarion	69	77	82	86	78	86 ± 7
Tama	93	77	85	96	88	93 ± 11
Sarpy	124	89	95	78	96	79 ± 13
Marshall	96	80	84	88	87	86 ± 8
Grundy	73	94	89	83	85	86 ± 8
Albaton	138	132	109	105	122	105 ± 12
Ida	62	104	92	72	83	81 ± 17
Weller	94	83	101	72	88	78 ± 18
Monona	39	47	53	77	54	73 ± 22

Table 20. (Continued)

Soil	Percent recovery of added S ppm S added					Percent recovery from regression mean
	7.5	15	22.5	30	Mean	
			Subsoils			
Clarion	92	91	95	76	88	79 ± 13
Webster	49	60	87	78	69	84 ± 14
Fayette	98	90	68	77	83	72 ± 15
Monona	85	93	89	81	87	84 ± 9
Weller	31	49	47	35	40	39 ± 11
Mean	82	84	84	80	82	81

and high values for the 7.5 ppm S treatment on the Sarpy soil and the 15 ppm S treatment on the Ida soil, would explain the excessively high recovery values given in Table 20.

Percent recovery of sulfur from five harvests of ryegrass was also obtained from the slope of the linear regression lines relating the yield of sulfur in ryegrass to the amount of sulfur added (Table 21). Considerable differences were found in some soils between percent recovery of sulfur calculated from the mean yields and those obtained by regression methods using adjusted yields from individual pots (Table 20). A 95 percent confidence interval about the mean percent recovery of applied sulfur, obtained from the linear regression lines, shows that there are no differences between soils with the exception of the Weller subsoil. The mean recovery of applied sulfur averaged over all soils except the Weller subsoil was 83 percent.

In the first harvest, the yield of sulfur response to applied sulfur was curvilinear (Figure 21) so that percent recovery of sulfur decreased with increasing amounts of sulfur added. Over all soils, recovery averaged 40, 30, 23 and 19 percent for the 7.5, 15, 22.5 and 30 ppm S rate respectively. Recovery over the first three harvests for all soils averaged 66 percent of the sulfur applied.

Table 21. Relationship between yield of sulfur in ryegrass from five harvests Y (mg S per kg soil) and sulfur applied X (ppm S) ("a" values were derived from the regression equations)

Soil	Lab. no.	Regression equation $Y = \alpha + \beta X$	Confidence interval on βs	"a" value	r^2
		Surface soils			
Hamburg	4	1.66	0.773 ± .072	2.2	.976
Hagener	3	1.09	0.789 ± .063	1.4	.986
Webster	2	5.33	0.761 ± .119	7.0	.946
Thurman	15	5.32	0.737 ± .096	7.2	.962
Dorset	16	5.32	0.873 ± .078	6.1	.982
Sharpsburg	8	5.74	0.867 ± .042	6.6	.994
Fayette	13	5.39	0.932 ± .060	5.8	.990
Clarion	1	5.72	0.864 ± .070	6.6	.985
Tama	12	6.07	0.934 ± .112	6.5	.968
Sarpy	11	8.89	0.788 ± .127	11.3	.944
Marshall	7	7.47	0.860 ± .084	8.7	.977
Grundy	9	10.33	0.857 ± .075	12.1	.982

Table 21. (Continued)

Soil	Lab. no.	Regression equation $Y = \alpha + \beta X$		Confidence interval on βs	"a' value	r^2
Albaton	10	13.45	1.048	± .116	12.8	.972
Ida	5	12.90	0.809	± .174	16.0	.905
Weller	14	15.66	0.777	± .176	20.2	.895
Monona	6	21.42	0.734	± .220	29.2	.830
			Subsoils			
Clarion	17	4.41	0.785	± .129	5.6	.942
Webster	18	3.05	0.839	± .144	3.6	.937
Fayette	20	6.37	0.723	± .154	8.8	.906
Monona	19	9.69	0.840	± .086	11.5	.977
Weller	21	26.16	0.389	± .111	67.2	.843
Mean		8.64	0.809		12.2	.947

"a" values "a" values for sulfur are an estimate of the amount of available sulfur in the soil in terms of the fertilizer S applied, that have provided the yield of sulfur in ryegrass, in the control treatments. The yield of sulfur values from each greenhouse pot were used to calculate "a" values. Sulfur yields were first adjusted for the contribution of sulfur derived from the basal layer of silica sand. The available sulfur content of the silica sand was determined by growing ryegrass in No. 10 cans filled with sand, to the stage where growth stopped, and the plants were dying as a result of sulfur deficiency. A sulfur-free nutrient solution was used at the same rates as in the main experiment, three harvests were made. Mean yields of dry matter, percent S in the dry matter, and yields of sulfur in ryegrass grown in silica sand are shown in Table 22.

Table 22. Yield of sulfur in ryegrass grown in silica sand (mean of three replicates)

Harvest	Yield dry matter (g/pot)	Percent S	Yield S (mg S/pot)
1	1.04	.451	4.69
2	1.59	.180	2.83
3	0.43	.126	0.54
Total	3.06		8.06

Yield of sulfur derived from the basal layer of silica sand was obtained by multiplying 8.06 mg S by the ratio of the weight of basal sand to the weight of silica sand which yielded 8.06 mg S. The values obtained were 2.68 mg S for the fine-textured soils, and 3.78 mg S for the coarse-textured soils.

The adjusted yields were then regressed on the weights of sulfur added and the resultant regression lines were used to calculate the "a" value. These were obtained for each soil from the relationship "a" = $-\frac{\alpha}{\beta}$, where α is the intercept of the regression line and β is the slope. The calculated "a" values, the intercept and slope of the regression lines are given in Table 21. All terms in the regression equation were divided by 1.5 so that yield of sulfur could be expressed in terms of mg S/kg soil (ppm) and β values (x 100) in terms of percent recovery of applied sulfur.

Experiment 2/68

The purpose of this greenhouse study was to determine the extent to which air-drying soil affected the availability of sulfur to plants. Earlier, in the laboratory study it was shown that air-drying increased the amount of sulfate sulfur extracted with either LiCl, $Ca(H_2PO_4)_2$ or $NaHCO_3$ by 1 to 3 ppm S. Several others, Freney (1958), Barrow (1961), Williams and Steinbergs (1964), and Williams

(1967b) have obtained similar increases of extractable sulfate with drying. It is not clear from their results as to whether the additional sulfate sulfur released on drying is entirely plant available. Williams and Steinbergs (1964) found a greater decrease in KH_2PO_4 extractable sulfur in air-dry soil after greenhouse cropping than occurred in field moist soils and concluded that the sulfur released by air-drying was available. According to Barrow (1961), organic sulfates are probably extracted after air-drying and become reduced to sulfide in the Johnson Nishita distillation procedure. These organic sulfates, however, may not be immediately available for plant uptake.

The six soils used in this experiment were dried for six days at 30° C, after which time, no further decrease in moisture content could be detected. The drying treatment was found to have an appreciable affect on the available nutrient status of the soils (Table 23). These results show, that air-drying more than doubled the anaerobic NH_4-N content and substantially increased exchangeable potassium and the sulfate sulfur extracted with 0.1 M LiCl. Available phosphorus and pH were not affected by air-drying.

Table 24 shows the effect of the drying treatment on the extractable sulfur in the soils and the yield of sulfur in ryegrass grown on those soils without added sulfur. In

Table 23. Effect of air-drying on the available nutrient content of soils used in Experiment 2/68

Soil	Lab. no.	pH (pp2m)		Anaerobic NH_4-N (pp2m)		P Bray No.1 (pp2m)		K exchangeable (pp2m)		S extractable (pp2m)	
		FM[a]	AD[b]	FM[a]	AD[b]	FM[a]	AD[b]	FM[a]	AD[b]	FM[a]	AD[b]
Hamburg	4	8.4	8.1	57	96	5	6	93	190	2.8	9.8
Sarpy	11	8.3	8.2	49	106	12	9	491	488	5.4	4.3
Webster	2	6.2	6.3	55	96	21	22	99	184	7.2	11.6
Marshall	7	7.9	7.7	35	93	26	31	246	369	8.8	10.4
Clarion	1	6.8	6.6	24	103	13	14	78	133	7.0	11.6
Tama	12	6.3	6.5	22	70	44	44	209	258	12.0	15.6
All soils		7.3	7.2	40	94	20	21	203	270	8.2	11.2

[a]FM = field moist sample,

[b]AD = air-dry sample.

These abbreviations will be used in subsequent tables in this dissertation.

Table 24. Effect of air-drying on the moisture status of the soils prior to potting, on sulfate sulfur extractable with 0.1 M LiCl and the yield of sulfur in ryegrass, on soils without added sulfur

Soil	Drying treatment	Moisture in soil at potting %	Field capacity %	Extractable S at potting (ppm)	Yield of S in control soil mg/kg soil
Hamburg	FM	24.4	25.3	1.4	1.67
	AD	1.5		4.8	3.03
Sarpy	FM	14.9	14.7	5.4	4.02
	AD	0.9		4.3	3.90
Webster	FM	18.1	30.1	3.6	4.04
	AD	2.8		5.8	3.92
Marshall	FM	21.6	28.4	4.4	4.08
	AD	2.3		5.2	5.26
Clarion	FM	15.4	21.7	3.5	4.90
	AD	1.5		5.8	6.27
Tama	FM	12.6	29.1	6.0	6.60
	AD	1.4		7.8	7.40

this experiment, drying of the soil resulted in changes in extractable S from 1.1 to 3.4 ppm with an average increase of 1.5 ppm extractable sulfate sulfur.

Dry matter yields

Average values for dry matter yield, percent sulfur and yield of sulfur in ryegrass are given for two harvests in Table 44 of the Appendix. Analysis of variance of the dry matter yields, Table 25, show that all the main effects, viz., blocks, soils, sulfur treatment, air-drying and harvests, were highly significant.

The highly significant effect of blocks was perhaps unexpected, since the entire experiment was conducted on one 18 x 3-1/2 foot greenhouse bench. However, in the northwest corner of the greenhouse, where the experiment was located, strong north to south temperature gradients have been observed during winter, which have resulted in marked growth differences in soybeans (Nnadi, personal communication). The temperature gradient appears to be due in part to the deflection of a current of warm air from the heating fans onto one end of the bench where this experiment was located. By using blocks in the design of this greenhouse experiment a considerable amount of variance has been removed from the error.

The highly significant response to applied sulfur shown for all soils in Figure 22 and for each soil in

Table 25. Analysis of variance of dry matter yield, in Experiment 2/68

Source of variation	df	Mean square	F
Blocks	1	.603	13.31**
Soils	5	5.146	113.60**
Sulfur	3	21.460	474.04**
Soil x sulfur	15	0.199	4.39**
Error (a)	23	0.045	
Drying	1	3.483	69.66**
Soil x drying	5	0.151	3.02*
Sulfur x drying	3	0.058	1.17
Soil x sulfur x drying	15	0.021	0.42
Error (b)	24	0.050	
Harvests	1	2.535	56.57**
Soil x harvest	5	0.506	11.29**
Sulfur x harvest	3	8.670	193.52**
Soil x sulfur x harvest	15	0.132	2.94**
Drying x harvest	1	0.090	2.01
Soil x drying x harvest	5	0.031	0.69
Sulfur x drying x harvest	3	0.014	0.31
Soil x sulfur x drying x harvest	15	0.027	0.61
Error (c)	48	0.045	
Total	191		

Figure 22. Effect of applied sulfur and air-drying of soils, on dry matter yield (average of six soils)

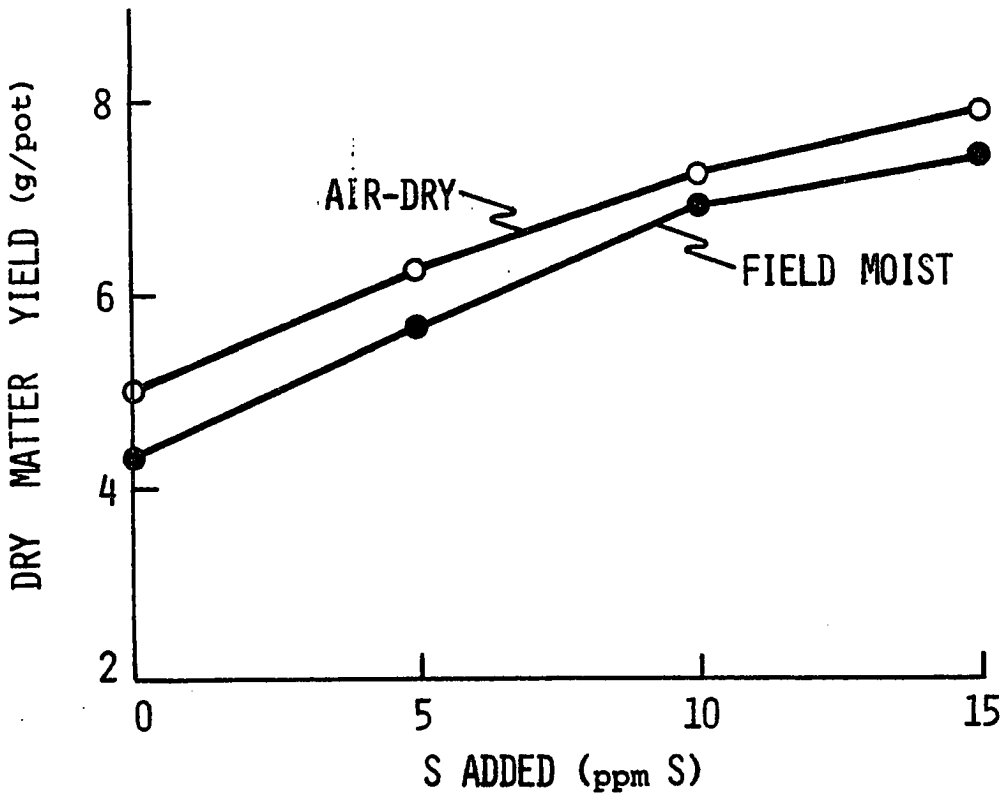
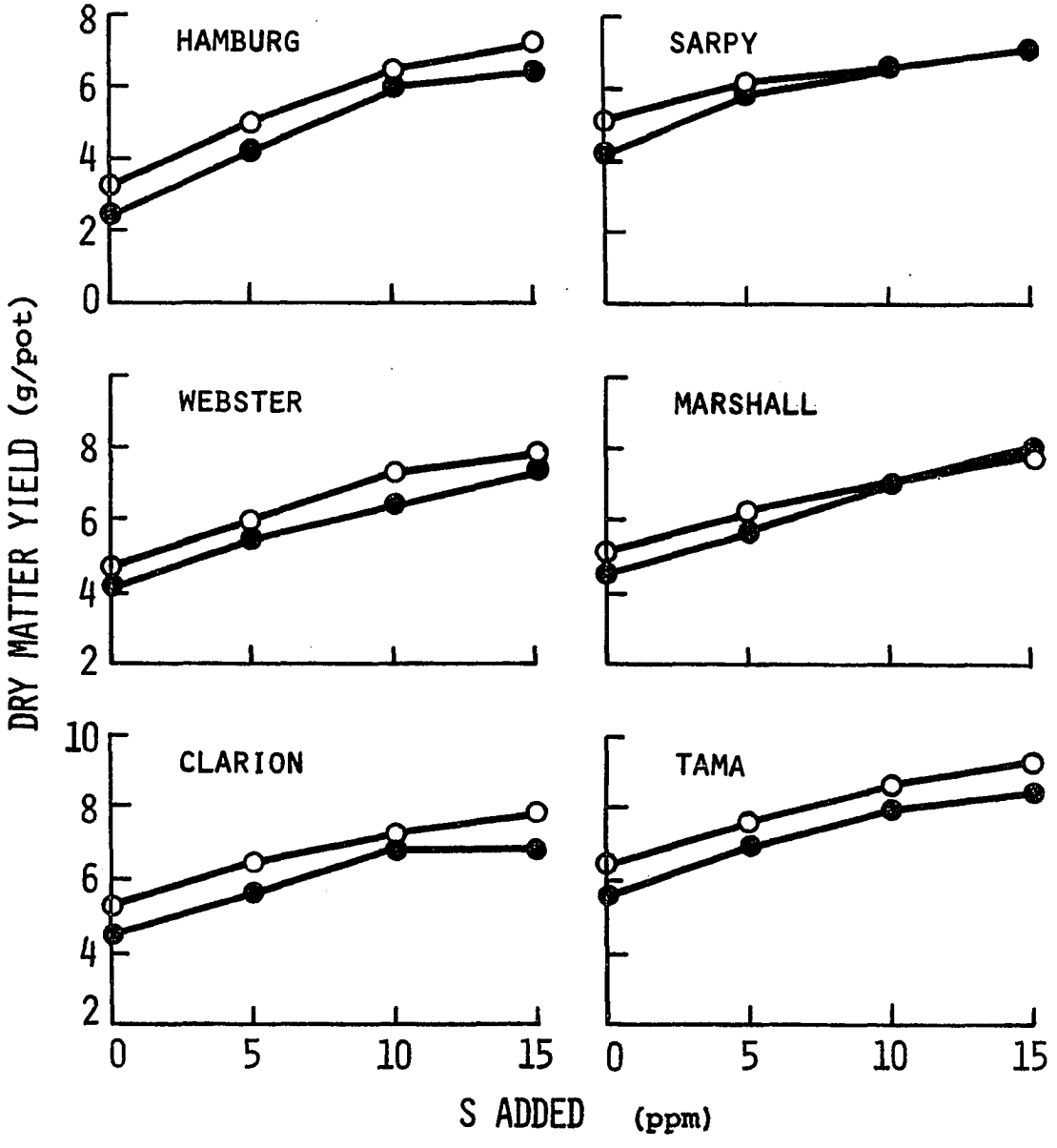

DRY MATTER YIELD (g/pot)
8
6
4
2
AIR-DRY
FIELD MOIST
0
5
10
15
S ADDED (ppm S)

Figure 23, is linear. Over all soils the linear effect accounted for 97.3 percent of the variance due to sulfur treatment.

The highly significant effect of soils is apparent in Figure 23 where soils such as Tama, because of a better supply of available sulfur and probably other nutrients as well, have yielded more dry matter than Hamburg and Webster. A significant soil by sulfur interaction indicates that the magnitude of the response to sulfur varies from soil to soil. Figures 23 shows that a greater response to sulfur was obtained on the Hamburg soil than on any of the other soils.

Of particular interest in this experiment was the highly significant effect of drying which is shown for all soils in Figure 22 and for soils individually, in Figure 23. Averaged over all soils air-drying gave a similar response at each level of applied sulfur. On individual soils the magnitude of the drying effect would appear to be equivalent to an addition of 2 to 3 ppm of available sulfur. The effect of harvest was large but was of lesser interest in this experiment. Averaged over all soils and sulfur levels, yields were lower in the second harvest. A highly significant sulfur by harvest interaction is explained by dry matter yields of the second harvest being lower at the 0 and 5 ppm S rate and higher at the

Figure 23. Effect of added sulfur and air-drying of soil on the yield of dry matter (solid circles, field moist soils and open circles, air-dry soils)


HAMBURG
SARPY
WEBSTER
MARSHALL
CLARION
TAMA
DRY MATTER YIELD (g/pot)
S ADDED (ppm)
0
2
4
6
8
10
0
5
10
15

10 and 15 ppm S rate than they were in the first harvest.

Percent S in ryegrass

The analysis of variance of percent sulfur in ryegrass, Table 26, shows the effects of blocks, soils, sulfur, harvest and the sulfur by harvest interaction to be highly significant. The highly significant block effect, attributed to a temperature gradient in the greenhouse, amounts to an average difference of 0.02 percent S between blocks one and two of the experiment. Differences between soils are small, as indicated by a small F value, and the average percent sulfur over all sulfur levels and harvests ranged from 0.19 percent S in Hamburg silt loam to 0.22 percent S in Tama silt loam. The response to sulfur was linear (the linear effect accounted for 97.3 percent of the sulfur effect), and averaged over all soils, ranged from 0.14 to 0.26 percent S.

The effect of drying was nonsignificant (F = 0.18) and because drying significantly increased dry matter yields, there is the possibility that the increased supply of N, K and possibly other nutrients with drying of the test soils have contributed also to the higher dry matter yields at all levels of applied sulfur. The effect of harvest was highly significant; percent sulfur in ryegrass decreased from an average of 0.25 percent S over all soils and rates of S in harvest 1 to 0.16 percent S in harvest 2.

Table 26. Analysis of variance of percent sulfur in ryegrass, in Experiment 2/68

Source of variation	df	Mean square	F
Blocks	1	0.02174	13.90**
Soils	5	0.00502	3.20*
Sulfur	3	0.12574	80.40**
Soil x sulfur	15	0.00195	1.25
Error (a)	23	0.00156	
Drying	1	0.00021	0.18
Soils x drying	5	0.00028	0.23
Sulfur x drying	3	0.00104	0.86
Soils x sulfur x drying	15	0.00089	0.73
Error (b)	24	0.00121	
Harvests	1	0.34637	310.11**
Soils x harvest	5	0.00268	2.39
Sulfur x harvest	3	0.01982	17.73**
Soils x sulfur x harvest	15	0.00188	1.69
Drying x harvest	1	0.00038	0.35
Soils x drying x harvest	5	0.00125	1.12
Sulfur x drying x harvest	3	0.00096	0.86
Soils x sulfur x drying x harvest	15	0.00173	1.55
Error (c)	48	0.00112	
Total	191		

The highly significant sulfur by harvest interaction is due to a greater decrease in percent sulfur with harvest at the higher rates of applied sulfur than at the lower rates (Table 27).

Table 27. Effect of harvest and applied sulfur on percent sulfur in ryegrass (average of six soils)

Harvest	Percent S in ryegrass S applied (ppm S) 0	5	10	15	Av.
1	.154	.242	.284	.314	.249
2	.127	.154	.163	.211	.164
Av.	.141	.198	.223	.263	

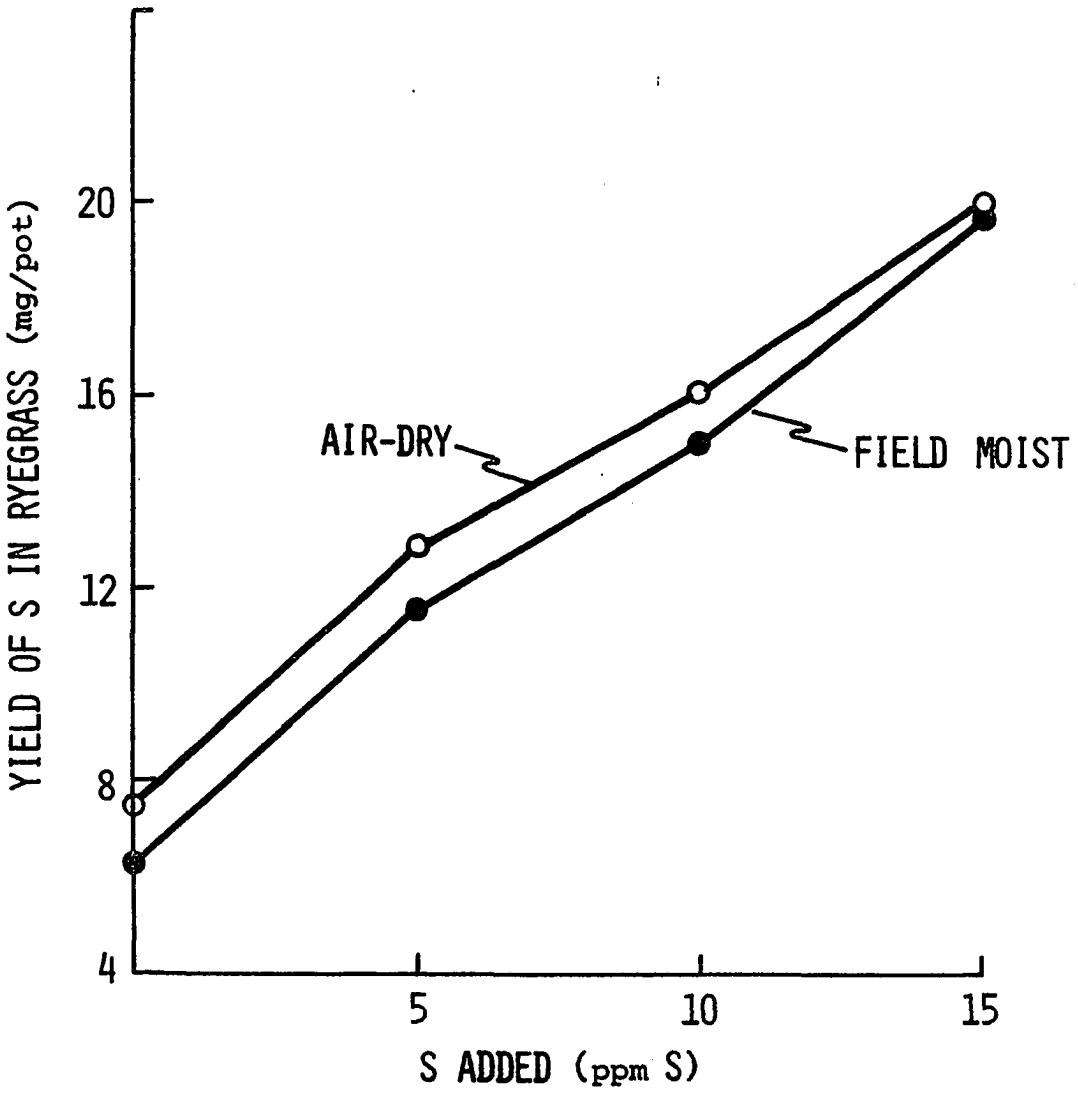
Yield of S in ryegrass

Analysis of variance in Table 28 shows that the main effects of blocks, soils, sulfur, air-drying and harvest were all highly significant. The significant effect of blocks has already been explained as being due to a temperature gradient in the greenhouse. Differences in sulfur yields between soils can be attributed to the amount of available sulfur present in the soil initially. The effect of added sulfur, shown in Figure 24, is linear (the linear effect accounted for 99 percent of the variance

Table 28. Analysis of variance of sulfur yield in ryegrass, in Experiment 2/68

Source of variation	df	Mean square	F
Blocks	1	42.1781	21.69**
Soils	5	40.2449	21.20**
Sulfur	3	363.7905	191.67**
Soil x sulfur	15	2.7769	1.46
Error (a)	23	1.8981	
Drying	1	10.2075	7.85**
Soil x drying	5	0.7077	0.54
Sulfur x drying	3	0.6497	0.50
Soil x sulfur x drying	15	0.7669	0.59
Error (b)	24	1.3013	
Harvests	1	459.8228	332.51**
Soil x harvest	5	14.8181	10.72**
Sulfur x harvest	3	10.3714	7.49**
Soil x sulfur x harvest	15	2.5175	1.82
Drying x harvest	1	0.0804	0.06
Soil x drying x harvest	5	1.5934	1.15
Sulfur x drying x harvest	3	1.0260	0.74
Soil x sulfur x drying x harvest	15	1.7593	1.27
Error (c)	48	1.3829	
Total	191		

Figure 24. Effect of applied sulfur and air-drying of soils on the yield of sulfur in ryegrass (average of six soils)


YIELD OF S IN RYEGRASS (mg/pot)
20
16
12
8
4
AIR-DRY
FIELD MOIST
5
10
15
S ADDED (ppm S)

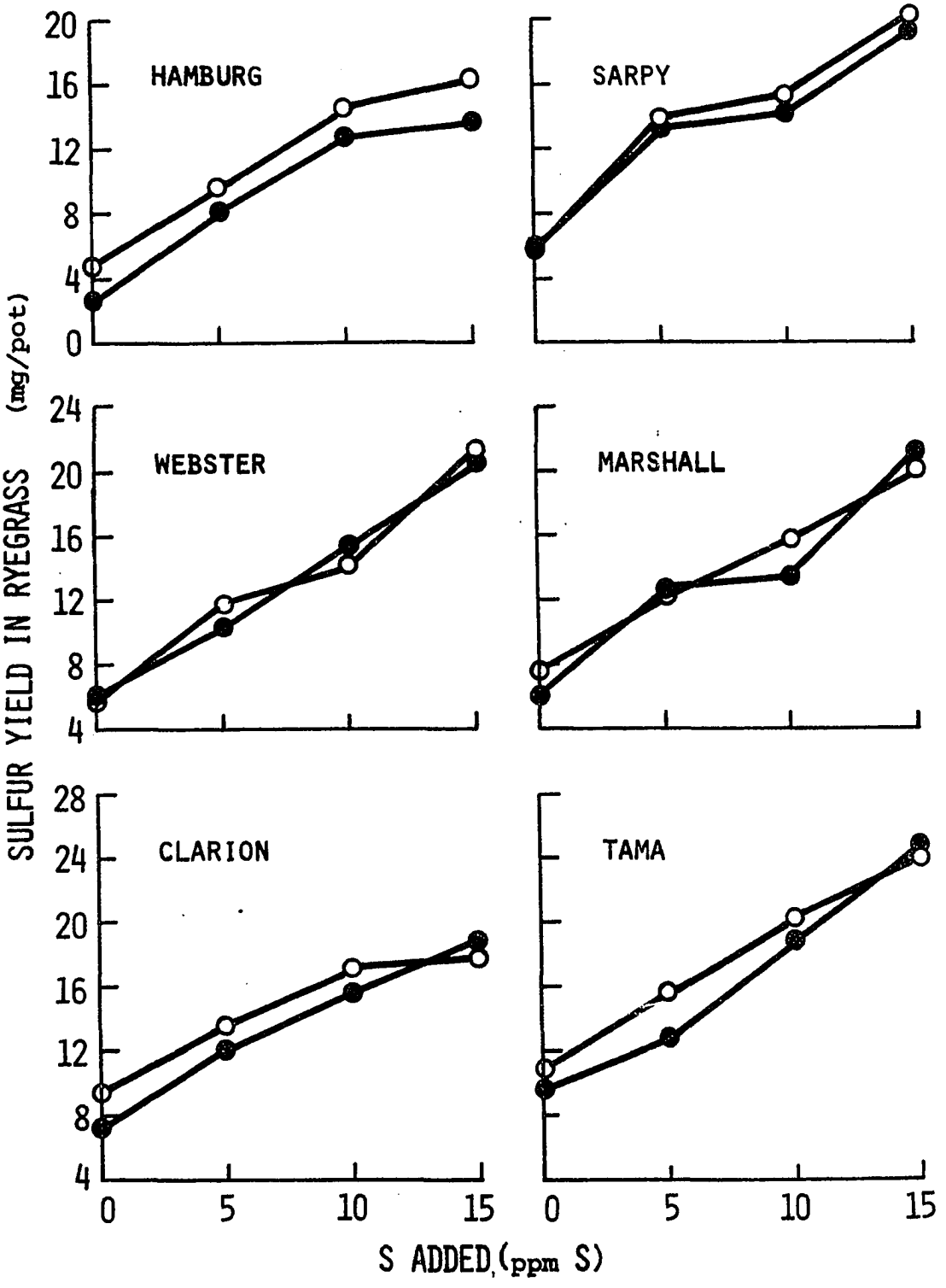
due to sulfur). The effect of air-drying soils is also shown in Figure 24, to have resulted in an increase in sulfur yield at all rates of applied sulfur except the highest. The effects of both sulfur and air-drying are shown for each soil in Figure 25. Interaction between soils, sulfur and drying, Table 28, was nonsignificant which means that in this experiment the drying and sulfur treatments both separately and together, had a similar effect of the yield of sulfur in ryegrass on each soil.

Yields of sulfur declined with harvest and the decline was much greater on the Tama soil than on the Hamburg or Sarpy soil.

Evaluation of Laboratory Indices of Extractable Sulfate Sulfur

Earlier in this chapter the results from a laboratory study were given, whereby the amounts of sulfate sulfur extracted from both air-dry and field moist soils by 0.1 M LiCl, $Ca(H_2PO_4)_2$ solution containing 500 ppm P, and 0.5 M $NaHCO_3$ at soil to solution ratios of 1:5 and 1:10 were compared. In order to determine the method of extraction that provided the best index of plant available sulfur, chemical values were evaluated in terms of sulfur taken up by ryegrass plants. A good chemical index of nutrient availability will extract an amount of that nutrient from the soil, which is proportional to the total that can be taken up by plants.

Figure 25. Effect of applied sulfur and air-drying of soils on yield of sulfur in ryegrass (solid circles, field moist soils and open circles, air-dry soils)


HAMBURG
SARPY
WEBSTER
MARSHALL
CLARION
TAMA
SULFUR YIELD IN RYEGRASS (mg/pot)
S ADDED (ppm S)
0
4
8
12
16
20
24
28
5
10
15

Linear correlation methods were used to examine the relationships between sulfate sulfur extracted chemically, and plant indices of available sulfur. The correlation matrix is given in Table 41, of the Appendix. Correlations among various methods used for obtaining extractable sulfur in soils have already been discussed in earlier sections. This section will be confined to relationships between sulfate sulfur extracted from soils in the laboratory (variables 1-12 of the matrix), and the plant indices unadjusted for sulfur contributed by silica sand (variables 18-27), obtained from the no sulfur treatments of the greenhouse experiment 1/68. Correlation coefficients of 0.433 and 0.549 are significant at the 5 percent and the 1 percent level respectively.

Sulfur uptake in the first harvest of ryegrass was highly correlated with sulfate sulfur extracted by LiCl (r ranged from .72 to .80 depending on air-drying and soil to extractant ratio), and less well correlated with sulfate sulfur extracted by phosphate (r ranged from .47 to .55). Correlations between sulfur uptake and sulfate sulfur extracted by $NaHCO_3$ were nonsignificant for harvest 1, harvests 1-3 and harvests 1-5 (r ranged from .26 to .32). Higher correlations were obtained when yields of sulfur from harvests 1-3 were related to sulfate sulfur extracted by LiCl or $Ca(H_2PO_4)_2$ (r ranged from 0.81 to 0.87 for LiCl

and from 0.69 to 0.78 for $Ca(H_2PO_4)_2$). The correlation was improved very little by including uptake of sulfur from harvests 4 and 5 (Table 29). This can be explained by reference to Figure 20 which shows that most of the total yield of sulfur was taken up from the control soils during the first three harvests. Moreover the correlation coefficient between yield of S in harvests 1-3 and that in harvests 1-5 was 0.992.

Correlation coefficients in Table 29 indicate slightly better relationships between uptake of sulfur in ryegrass with sulfate sulfur extracted from air-dry soils than with sulfate sulfur extracted from field moist soils. Possibly the additional sulfate sulfur extracted by LiCl or $Ca(H_2PO_4)_2$ after air-drying was potentially available to plants in undried soils in the greenhouse.

The highest correlations between sulfur uptake in ryegrass over five harvests and sulfate sulfur extracted by the three extractants LiCl, $Ca(H_2PO_4)_2$ and $NaHCO_3$ are shown in Figures 26, 27 and 28. The relationship between sulfur uptake in ryegrass and HI-reducible sulfur is also shown in Figure 28. Because there is no significant relationship between plant uptake of sulfur and either $NaHCO_3$ extractable or HI-reducible sulfur, regression lines have been omitted.

The regression equations and correlation coefficients

Table 29. Relationship between yield of sulfur in ryegrass (Y), from soils where sulfur was not applied and sulfate sulfur extracted with 0.1 M LiCl (X)

Extraction treatment	Regression equation	X intercept	Correlation coefficient (r)
	Yield of S (mg/kg soil) Harvest 1		
FM, 1:5	Y = 0.94X + 0.67	- 0.71	0.72
AD, 1:5	Y = 0.89X - 0.41	0.35	0.76
FM, 1:10	Y = 0.77X + 0.98	- 1.28	0.72
AD, 1:10	Y = 0.78X + 0.63	0.80	0.80
	Yield of S (mg/kg soil) Harvests 1-3		
FM, 1:5	Y = 1.86X - 1.08	0.58	0.81
AD, 1:5	Y = 1.72X - 2.82	1.64	0.83
FM, 1:10	Y = 1.58X - 0.88	0.56	0.84
AD, 1:10	Y = 1.52X - 3.43	2.34	0.87
	Yield of S (mg/kg soil) Harvests 1-5		
FM, 1:5	Y = 2.37X - 1.90	0.80	0.81
AD, 1:5	Y = 2.20X - 4.30	1.95	0.84
FM, 1:10	Y = 2.03X - 1.83	0.93	0.85
AD, 1:10	Y = 1.93X - 4.93	2.55	0.87

for some of the better relationships between sulfur uptake in the plant and sulfate sulfur extracted from the soil with 0.1 M LiCl, are given in Table 29. The regression coefficients provide a measure of the relative availability of the extractable sulfate to the plants. The regression coefficients for the first harvest indicate that most of the sulfate extracted was available to the ryegrass.

Figure 26. Relationship between sulfur uptake by ryegrass in five harvests and sulfate sulfur extracted by 0.1 M LiCl, on air-dry soils, using a 1:10 soil to extractant ratio

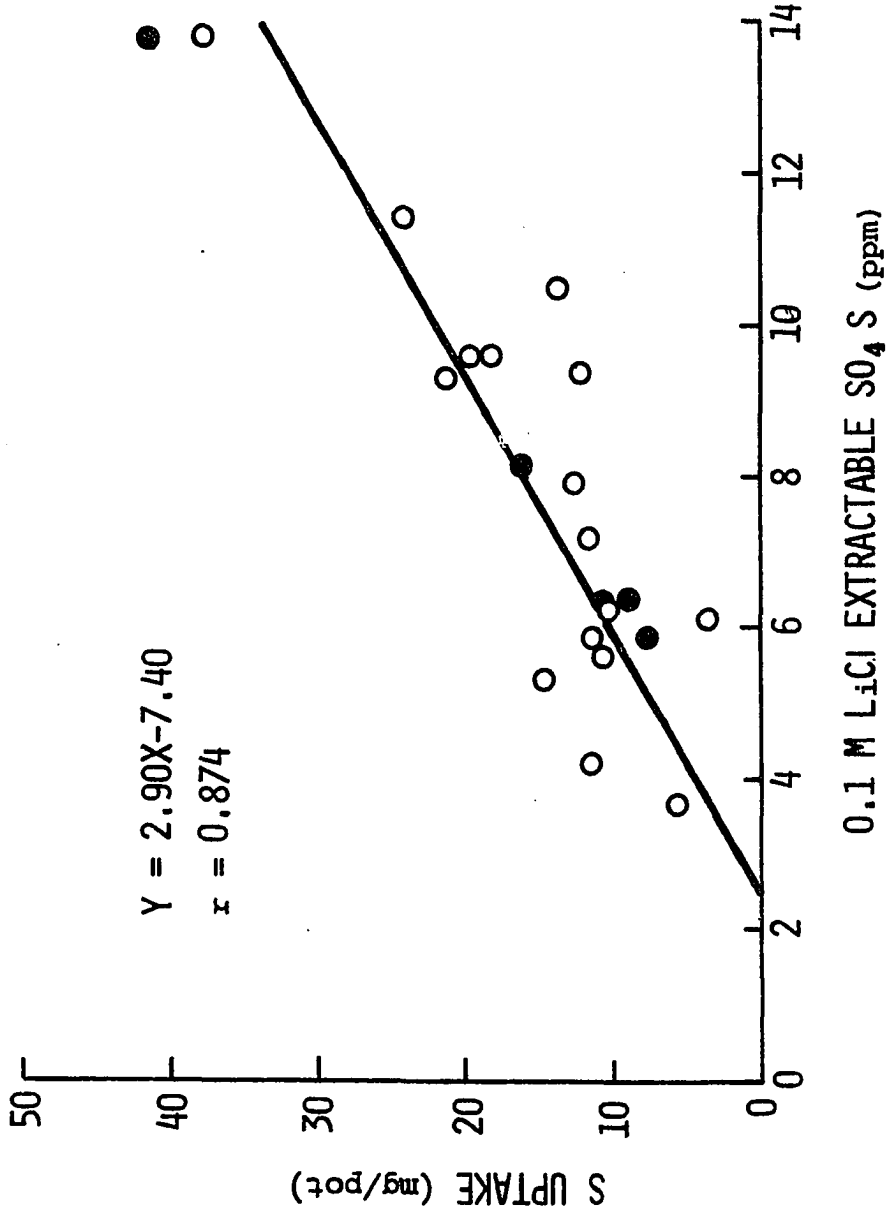

Y = 2.90X-7.40
r = 0.874
S UPTAKE (mg/pot)
0.1 M LiCl EXTRACTABLE SO_4 S (ppm)
0
10
20
30
40
50
0
2
4
6
8
10
12
14

Figure 27. Relationship between sulfur uptake by ryegrass in five harvests and sulfate sulfur extracted by $Ca(H_2PO_4)_2$ solution, on air-dry soils, using a 1:5 soil to extractant ratio

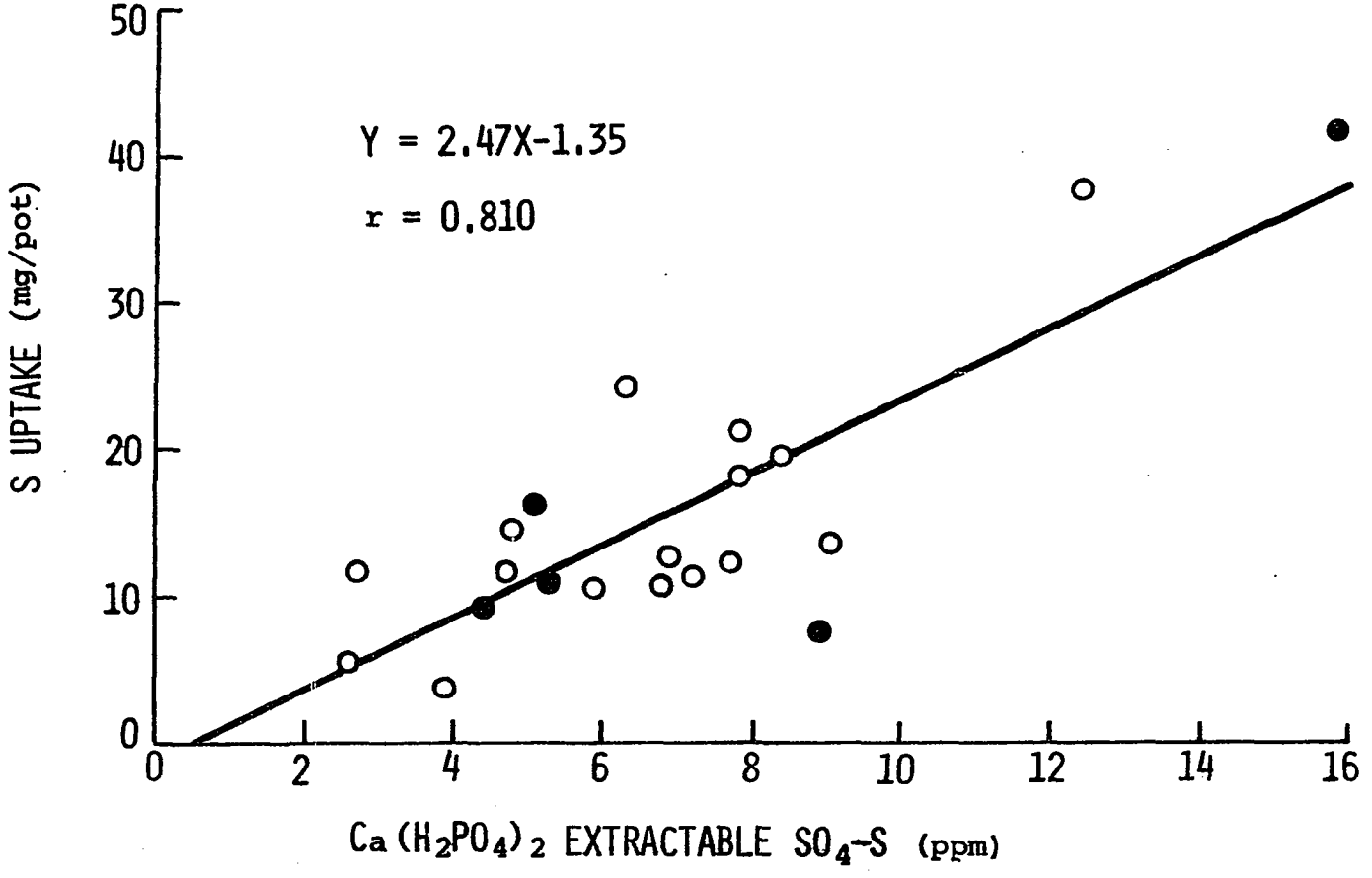
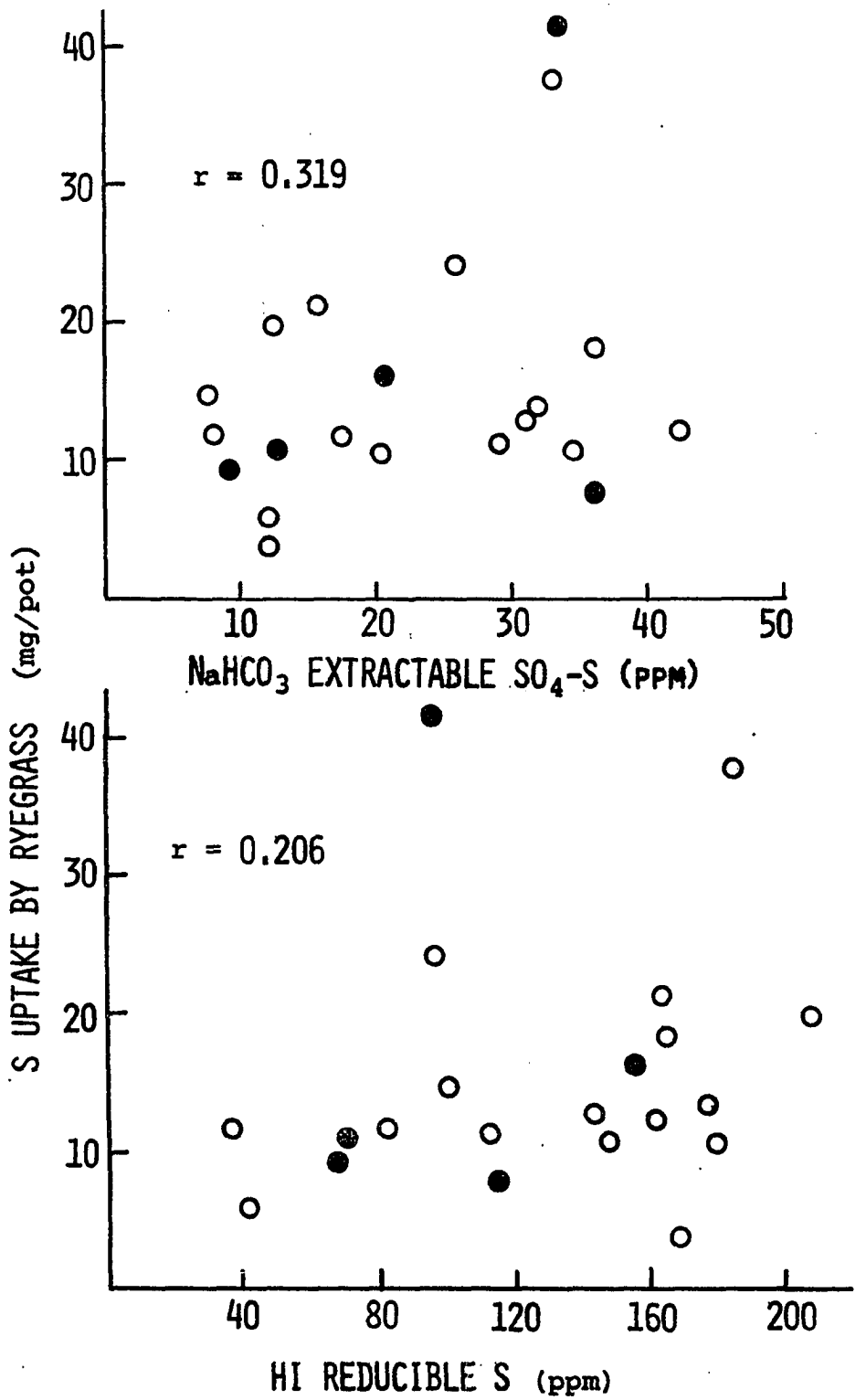

Y = 2.47X-1.35
r = 0.810
S UPTAKE (mg/pot)
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
Ca (H2PO4)2 EXTRACTABLE SO4-S (ppm)

Figure 28. Relationship between sulfur uptake by ryegrass in five harvests and sulfate sulfur extracted by (a) 0.5 M $NaHCO_3$ and (b) HI and other reducing acids


r = 0.319
40
30
20
10
10
20
30
40
50
NaHCO3 EXTRACTABLE SO4-S (PPM)
S UPTAKE BY RYEGRASS (mg/pot)
r = 0.206
40
30
20
10
40
80
120
160
200
HI REDUCIBLE S (ppm)

However, for harvests 1-3 and 1-5 regression coefficients indicate that from 1.5 to more than twice the amount of sulfur extracted by LiCl was taken up by ryegrass plants. The X intercepts given in Table 29 provide an indication of the extractable sulfate in soil which is not available to the plant. These values tend to be higher for air-dry soils, than for soils extracted in the field moist condition. Thus although the effect of air-drying has been to increase by 1-3 ppm the sulfate extracted from soils, a fraction of the sulfate extracted does not appear to be plant available. These could well be organic sulfates that would contribute to the sulfate measured in the soil and yet not be readily available to the plant.

Generally, yield of sulfur in ryegrass correlated better with sulfur extracted, than did either percent sulfur or dry matter yield. Correlations between dry matter yield and sulfate extracted by LiCl were low in the first harvest and nonsignificant with $Ca(H_2PO_4)_2$, because initially, plant growth was dependent more on the available nitrogen content of the soil than it was on the sulfur status. In subsequent harvests, differences due to nutrients other than sulfur were minimized, and correlations between dry matter yield and sulfate sulfur extracted were almost as high as those for yield of sulfur. This is to be expected for as shown in the correlation matrix,

Table 41 of the Appendix, dry matter yield and sulfur yield were very highly correlated.

Correlations between percent sulfur in ryegrass and chemically extractable sulfate sulfur, initially, are better than those between dry matter yield and extractable sulfur. As successive harvests depleted the available sulfur in the soil, the percent sulfur in the plant fell to a deficiency level, which tended to be uniform from soil to soil. As a result, with increasing number of harvests the correlation coefficient declined.

Correlation between "a" values and sulfate sulfur extracted by either LiCl, Figure 29a, or $Ca(H_2PO_4)_2$ (Table 30) were not as high as those obtained with sulfur uptake in ryegrass from the no sulfur treatment for either harvests 1-3 or 1-5. For LiCl, extractable sulfate sulfur, values ranged from 0.72 to 0.79 and with $Ca(H_2PO_4)_2$ from 0.76 to 0.81. The correlation between "a" values and yield of sulfur in ryegrass in the no sulfur treatments were 0.59, 0.88 and 0.90 for harvests 1, 1-3, and 1-5, Figure 29b, respectively. Good correlations were obtained between "a" values and yield of sulfur over several harvests because "a" values have been calculated from yield of sulfur data. In Figure 29b the y intercept corresponds to a value of 2.4 mg S per 1000 g/soil which is interpreted as being the uptake of sulfur in the plant when the "a" value was

Figure 29. Relationship between "a" values and (a) LiCl extractable sulfate sulfur and (b) S uptake in ryegrass, in five harvests

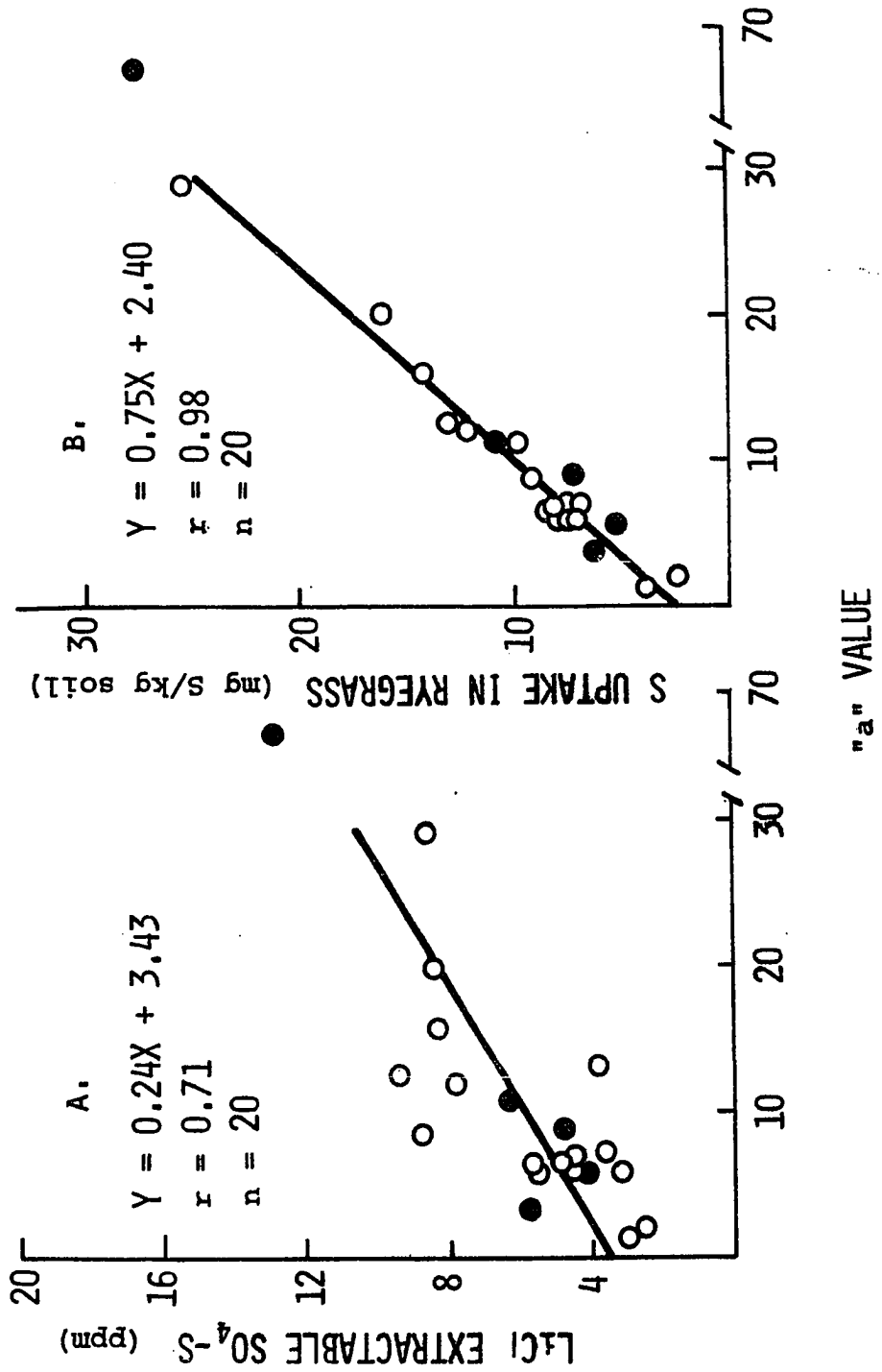

A.
Y = 0.24X + 3.43
r = 0.71
n = 20
B.
Y = 0.75X + 2.40
r = 0.98
n = 20
LiCl EXTRACTABLE SO4-S (ppm)
S UPTAKE IN RYEGRASS (mg S/kg soil)
"a" VALUE
20
16
12
8
4
30
20
10
70
30
20
10

Table 30. Relationships between "a" value (Y) and sulfate sulfur extracted with 0.1 M LiCl and $Ca(H_2PO_4)_2$ solution (X)

Extraction treatment	Regression equation	Correlation coefficient (r)
	"a" value (ppm S)	
0.1 M LiCl		
FM, 1:5	Y = 4.85X - 13.01	0.74
AD, 1:5	Y = 4.30X - 16.25	0.72
FM, 1:10	Y = 4.23X - 13.19	0.79
AD, 1:10	Y = 3.69X - 17.04	0.74
$Ca(H_2PO_4)_2$		
FM, 1:5	Y = 4.06X - 9.55	0.79
AD, 1:5	Y = 3.69X - 13.16	0.81
FM, 1:10	Y = 3.69X - 9.96	0.76
AD, 1:10	Y = 3.33X - 14.17	0.79

zero. This is approximately the amount of sulfur that was contributed by the silica sand which formed the basal layer of the pot culture. The regression coefficient gives an estimate of the fraction of the available sulfur in soil that was removed after seven months cropping in the greenhouse. It is believed that nearly all the available sulfur was removed by the ryegrass plants and that the difference between the total removed and that measured in five harvests of leaves, remained in the stubble and the root system of the ryegrass plants. The stubble was not analyzed for

sulfur and hence a complete balance sheet cannot be compiled.

Estimate of Mineralization of Organic Sulfur

Soil samples taken from greenhouse pots immediately after harvest 5, were stored moist at 3° C until they were extracted with 0.1 M LiCl for sulfate sulfur. In this study only soils which had not received gypsum were used, and prior to extraction they were passed through a 2 mm sieve.

The amounts of sulfate sulfur extracted by LiCl from field moist samples before and after cropping are shown in Table 31. The values given for each soil after cropping, are mean values of three replicates from the no-sulfur treatments. The difference between the sulfate sulfur extracted before and after cropping is assumed to be the amount of water soluble sulfate taken up by the plants.

Cropping reduced the level of sulfate sulfur by an average of 4.6 ppm S, with a range of 0.1 to 10.0 ppm S for the Hamburg and Weller (18-24 in) soils respectively. The decrease in sulfate sulfur with cropping is highly correlated with S uptake in the first harvest of ryegrass (Figure 30). The regression coefficient for this relationship indicates that sulfur yield in the ryegrass tops harvested accounts for an average of 72 percent of the sulfate sulfur that was removed from the soil over the entire seven month cropping period. Exceptions to this

Table 31. Decrease in LiCl extractable sulfate sulfur in untreated soils, undried after cropping compared with sulfur uptake in ryegrass

Soil	LiCl extractable SO_4-S (ppm)[a]		
	Before cropping	After cropping	Decrease
Hamburg	2.0	1.9	0.1
Hagener	1.6	1.1	0.5
Webster	3.2	0.6	2.6
Thurman	3.3	0.2	3.1
Dorset	5.3	0.6	4.7
Sharpsburg	4.0	0.5	3.5
Fayette	3.6	0.7	2.9
Clarion	4.6	0.9	3.7
Tama	5.1	0.7	4.4
Sarpy	3.4	0.4	3.0
Marshall	7.4	0.6	6.8
Grundy	5.7	0.3	5.4
Albaton	7.9	1.3	6.6
Ida	7.4	0.7	6.7
Weller	5.8	0.8	5.0
Monona	7.9	0.9	7.0

[a]Sulfate sulfur extracted from undried soils at a soil:extractant ratio of 1:5.

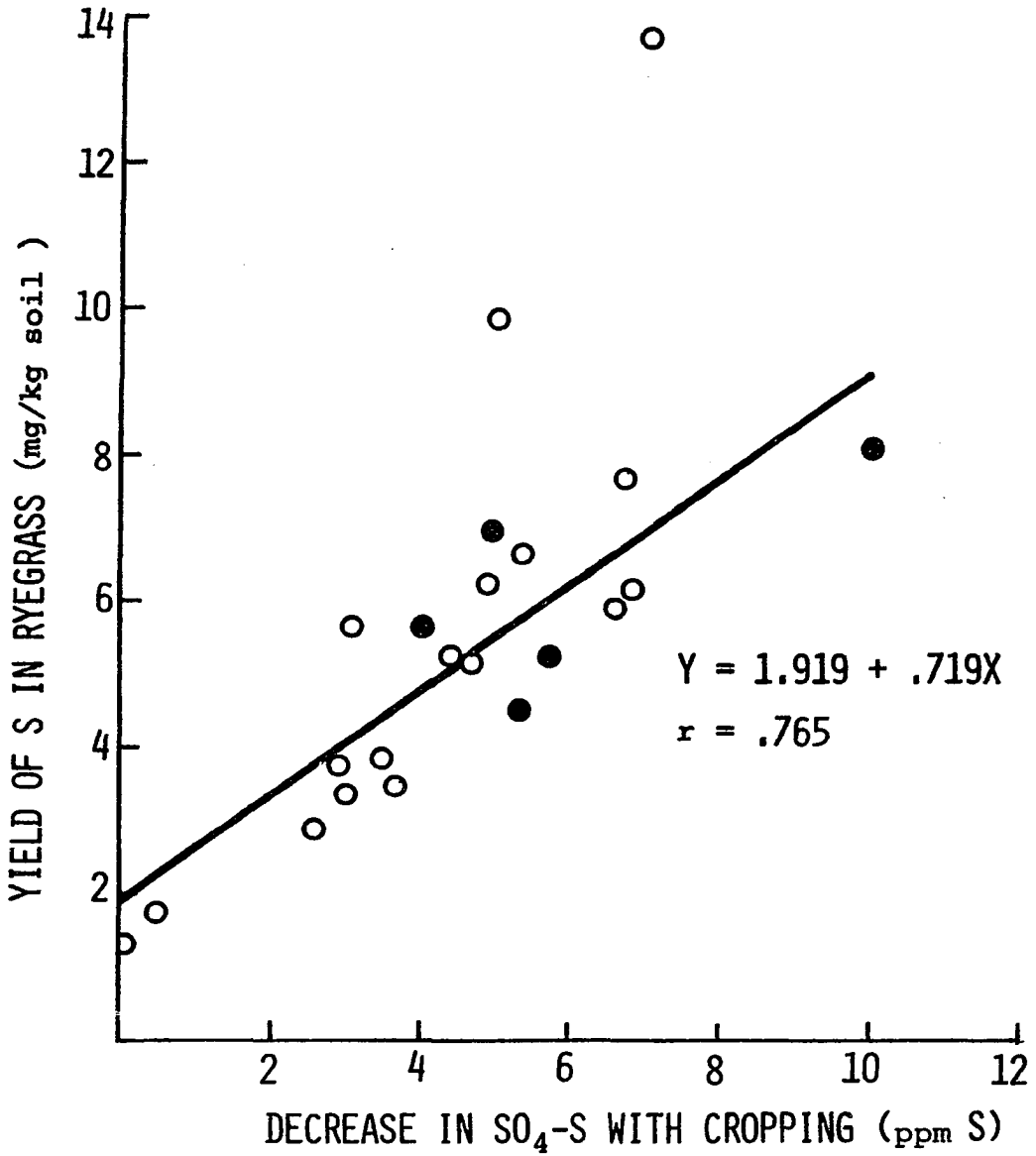
Yield of S in ryegrass mg S/kg soil	S mineralized	
	mg S/kg soil	% total S
0.71	0.61	0.22
1.28	0.78	1.00
5.20	2.62	0.78
5.33	2.23	3.30
5.34	0.64	0.38
5.38	1.88	0.71
5.77	2.87	1.40
6.50	2.80	0.99
6.79	2.39	1.00
7.23	4.23	2.00
7.48	0.68	0.23
10.30	4.90	1.70
11.40	3.80	0.84
12.42	5.72	1.91
14.42	9.42	5.00
23.45	16.45	4.95

Table 31. (Continued)

Soil	LiCl extractable SO_4-S (ppm)[a]		
	Before cropping	After cropping	Decrease
Clarion	5.5	0.2	5.3
Webster	5.9	0.2	5.7
Fayette	4.1	0.1	4.0
Monona	5.0	0.1	4.9
Weller	10.4	0.4	10.0
Mean	5.2	0.6	4.6

Yield of S in ryegrass mg S/kg soil	S mineralized	
	mg S/kg soil	% total S
3.51	- 1.79	-
4.46	- 1.24	-
5.38	1.38	1.58
9.08	4.18	1.99
25.87	15.87	11.82
8.44	3.82	2.2

Figure 30. Relationship between the decrease in LiCl extractable sulfate sulfur with cropping, and the sulfur yield in ryegrass at harvest 1


YIELD OF S IN RYEGRASS (mg/kg soil)
14
12
10
8
6
4
2
2
4
6
8
10
12
DECREASE IN SO_4-S WITH CROPPING (ppm S)
Y = 1.919 + .719X
r = .765

relationship are the Monona, and Ida soils which have contributed to the first crop of ryegrass much more sulfur than could be extracted using 0.1 M LiCl. Because the phosphate extractant failed to remove any additional sulfate from these soils it may be concluded that the additional sulfur in the plant came from mineralization of organic sulfur during the first few weeks of the experiment. If a substantial part of the water soluble sulfate was removed in the first harvest as shown in Figure 30, then subsequent growth of ryegrass must have been dependent on mineralization of organic sulfur together with a contribution from the basal layer of silica sand and possibly sulfur absorbed by plants and soil from the atmosphere. In Figure 30 the y intercept was 1.9 mg S which can be interpreted as sulfate derived from the sand layer and from the atmosphere.

Sulfate sulfur remaining in the soil after cropping, averaged 0.6 ppm with a range of 0.1 to 1.9 ppm. This residual sulfate sulfur was extremely low in subsoils and with some of the subsoil determinations, the level of sulfate present was below the limit of detection.

An estimate of the sulfur mineralized from soil in which plants were growing, was made by deducting from the sulfur taken up by plants the contribution from the silica sand and the decrease of LiCl extractable sulfate sulfur

in the soil over a seven month cropping period. These estimated values, shown in Table 31, are expressed as mg S/kg soil and also as a percentage of the total sulfur in the soil. An average of 3.82 mg S/kg soil (ppm) was mineralized with a range of -1.79 to 16.45 ppm S.

Whereas in most soils, more sulfur was recovered in ryegrass tops over five harvests than could be accounted for by a decrease of extractable sulfate in soil, ryegrass grown on two of the subsoils took up an amount of sulfur that was smaller than the decrease in LiCl extractable sulfate sulfur. Such a reduction in the inorganic sulfate sulfur content of soils has been attributed by Freney and Spenser (1960) to immobilization by rhizosphere micro-organisms.

The residual sulfate sulfur extractable with LiCl, at a 1:5 ratio, was also determined for five soils on which the 15 and 30 ppm sulfur treatments had been applied. The mean sulfate sulfur values from the three replicates of each treatment, are shown in Table 32 together with the mean yield of sulfur in ryegrass from the fifth harvest. Table 32 shows that after five harvests most of the sulfate sulfur had been removed from the Webster, Sharpsburg and Fayette soils. Sulfur yields in the fifth harvest were consistent with the low levels of sulfate sulfur remaining in the soil. In the Monona surface soils and Weller sub-

Table 32. LiCl extractable sulfate sulfur in soils, after harvest 5 and sulfur uptake in ryegrass, at harvest 5

Soil	Depth (in)	LiCl extractable SO_4-S (ppm)				S uptake in harvest 5 mg/pot		
		Before cropping	After cropping					
		ppm S added						
		0	0	15	30	0	15	30
Webster	0-6	3.2	0.5	0.6	0.4	0.6	0.7	1.6
Sharpsburg	"	4.0	0.5	0.5	0.4	0.9	1.0	3.0
Monona	"	7.9	0.9	1.4	3.7	2.8	2.4	8.2
Fayette	18-24	4.1	0.1	0.3	0.1	0.5	0.3	1.5
Weller	"	10.4	0.4	1.7	4.5	2.7	6.4	7.1

soil, considerable sulfate sulfur still remained in the soils where 30 ppm of S had been applied and sulfur yields were consistently higher over all levels of applied sulfur.

Time and Depth of Sampling Study

This study, designated Experiment 3/69, was undertaken to obtain information on the distribution of sulfate sulfur with depth and time in some representative Iowa soils. Although most studies of the sulfate-sulfur status of soil have been confined to the plow layer, some recent work by Sanford and Lancaster (1962), Roberts and Koehler (1968) and Blakemore et al. (1968) has been concerned with the sulfate sulfur status of subsoils as well. Very little information is available on the distribution of sulfate sulfur in soil with time.

Water soluble sulfate is the principle form of sulfur available to plants in many soils (Reisenauer, 1967) and the sulfate concentration in soils would be expected to vary during the growing season, in a manner similar to that of nitrate nitrogen. Thus sulfate sulfur, during the growing season, would be depleted by plant uptake and by leaching beyond the root zone, and would be replenished by mineralization of organic sulfur and accessions of sulfur from the atmosphere.

At each of six sites, a sampling area 30 feet square was marked out and divided into four plots, each 15 feet

square. A composite sample consisting of four cores was taken from each of the four plots for five depths down the profile viz., 0 to 6, 6 to 12, 12 to 24, 24 to 36 and 36 to 48 inches below the soil surface. Each site was sampled three times during 1969, in May at corn planting, in August just after silking, and in November after harvest. Four of the sites were planted to corn, one was in native pasture and one was fallowed. Preparation of these samples for analysis has already been described in the Experimental Materials and Methods chapter. Two of the four composite samples from each site, at each time of sampling, were analyzed for sulfate sulfur extracted with 0.1 M LiCl.

Some chemical characteristics for each of the soils sampled down the profile are given in Table 45 of the Appendix. All soils were very moist at the time of first sampling and a water table was encountered at about 24 inches in both the Hagener and Webster soils. Both Clarion and Webster soils had higher organic carbon contents which extend deeper into the profile than did organic carbon in the loess soils. Three of the soils were calcareous in the subsoil, with pH values greater than 8.0; the other soils range from pH 6.1 to 6.8. Available phosphorus was extremely low on the calcareous Hamburg soil and decreased sharply in the calcareous Webster and Clarion subsoils. The Bray No. 1 extractant (0.025 N HCl and 0.03 N NH_4F)

has been shown, by Koswara and Hanway (1969) to be rather an ineffective extractant of available phosphorus on calcareous soils; with $CaCO_3$ present in soil the HCl of the extractant is neutralized and phosphorus is precipitated as calcium phosphate. The sulfate sulfur levels, shown in Table 45, do not appear to be related to any of the other chemical characteristics shown.

Sulfate sulfur extracted by 0.1 M LiCl from air-dry soil is shown for six soils at five depths and for three times of sampling in Table 33. The analysis of variance, Table 34, shows that the effects of soils, depths, time of sampling and the soil by depth interaction on extractable sulfur were highly significant.

Differences due to soils were large, and are shown in Table 33 to range from an average, over the 48 inch depth, of 1.9 ppm S on the Hagener soil to 6.1 ppm S on the Clarion soil. Over all soils, differences in sulfate extracted existed between depths, but no trends are apparent. On individual soils, however, differences in sulfate content with depth are evident. Extractable sulfate in the Sharpsburg soil, for example, declines with depth whereas in the Webster and Hagener soils, both with a high water table, the extractable sulfate was remarkably constant with depth.

Besides major differences in sulfate sulfur contents between soils, differences due to time of sampling are a

Table 33. Extractable sulfate sulfur in soils according to depth and time of sampling, in Experiment 3/68

Soil	Depth (in)	Extractable S (ppm)			
		May	August	November	Mean
Hamburg	0-6	6.0	4.6	4.6	5.1
	6-12	3.1	2.7	3.1	3.0
	12-24	4.6	4.5	2.6	3.9
	24-36	6.6	6.3	5.0	5.9
	36-48	6.2	5.7	4.6	5.5
	Av.	5.3	4.8	4.0	4.7
Hagener	0-6	2.4	1.8	1.6	2.0
	6-12	2.4	1.9	1.9	2.1
	12-24	1.7	1.4	1.7	1.6
	24-36	2.5	1.9	1.0	1.8
	36-48	2.7	2.0	1.9	2.2
	Av.	2.3	1.8	1.6	1.9
Webster	0-6	10.3	4.2	4.7	6.4
	6-12	7.0	5.0	3.8	5.3
	12-24	4.6	5.4	4.4	4.8
	24-36	6.3	5.7	5.6	5.9
	36-48	7.3	5.0	5.8	6.1
	Av.	7.1	5.1	4.9	5.7

Table 33. (Continued)

Soil	Depth (in)	Extractable S (ppm)			
		May	August	November	Mean
Sharpsburg	0-6	5.6	3.8	3.4	4.3
	6-12	4.3	3.2	3.5	3.7
	12-24	3.8	2.4	2.5	2.9
	24-36	2.6	2.4	1.3	2.1
	36-48	1.7	2.1	0.9	1.6
	Av.	3.6	2.8	2.4	2.9
Fayette	0-6	4.1	5.8	5.4	5.1
	6-12	6.4	2.5	3.2	4.0
	12-24	5.3	3.9	5.7	5.0
	24-36	3.4	3.6	3.7	3.6
	36-48	2.3	2.7	1.9	2.3
	Av.	4.3	3.7	4.0	4.0
Clarion	0-6	6.8	5.9	4.3	5.7
	6-12	5.8	6.5	4.8	5.7
	12-24	7.3	5.9	4.9	6.1
	24-36	9.4	7.6	5.3	7.4
	36-48	6.1	6.0	5.1	5.7
	Av.	7.1	6.4	4.9	6.1
All soils	0-48	5.0	4.1	3.6	

Table 34. Analysis of variance of extractable sulfate sulfur in soils, sampled over depths and times, in Experiment 3/68

Source of variation	df	Mean square	F
Soil	5	77.7047	63.44**
Depth	4	5.0088	4.09**
Soil x depth	20	5.0868	4.15**
Time	2	27.6270	22.55**
Soil x time	10	2.1677	1.77
Depth x time	8	0.8712	0.71
Soil x depth x time	40	1.6959	1.38
Error	90	1.2249	
Total	179		

most important feature of this study. Over all soils and depths, Table 33 shows that extractable sulfate declined from 5.0 ppm S in May to 3.6 ppm in November. This decrease of 1.4 ppm while not large, represents over a 48 inch soil depth, a loss of 21 lbs. of sulfur per acre. On individual soils the decrease over the growing season ranged from 2.2 ppm S for both the Clarion and Webster soils to as little as 0.3 ppm on the Fayette soil. The soil by time interaction, however, did not reach significance at the 5 percent

level.

Using the data given in Table 33, an estimate was made of the average sulfate sulfur content of each soil to a depth of 48 inches, during the 1969 growing season, Table 35. The calculation of the amount of sulfate sulfur in the profile is based on the assumptions, that a 6 inch slice of soil weighs 2 x 10^6 lb. per acre, that the bulk density of each soil was 1.32 g/cc, and that the bulk density remains constant with depth. While the bulk density of the Sharpsburg, Fayette, Clarion and Webster soils may lie close to 1.32, the Hamburg soil under grassland will be closer to 1.00 and the Hagener loamy sand will be closer to 1.50. Consequently, by assuming the same bulk density for each soil, the sulfate sulfur content of the Hagener profile is probably underestimated and that of the Hamburg profile, overestimated.

With these reservations concerning the validity of the data, it is apparent that the Clarion and Webster soils contain considerably more sulfate sulfur than do the loess soils Hamburg, Fayette and Sharpsburg or the sandy Hagener soil. In spite of these differences in sulfur supplying capacity between soils, there would appear to be adequate available sulfur present for the needs of most crops. In fact, the sulfur needs of both corn and soybeans, which ranges between 15 and 25 lb. S per acre for both grain and

Table 35. An estimate of extractable sulfate sulfur in the root zone of six Iowa soils

Depth (in)	LiCl extractable sulfur (lb. per acre)					
	Hagener	Sharpsburg	Fayette	Hamburg	Webster	Clarion
0-6	4.0	8.6	10.2	10.2	12.8	11.4
6-12	4.2	7.4	8.0	6.0	10.6	11.4
12-24	6.4	11.6	20.0	15.6	19.2	24.4
24-36	7.2	8.4	14.4	23.6	23.6	29.6
36-48	8.8	6.4	9.2	22.0	24.4	22.8
0-48	30.6	42.4	61.8	77.4	90.4	99.6

stover (Tisdale and Nelson, 1966), can be met from the sulfate sulfur content of the top 24 inches of soil.

GENERAL DISCUSSION

Sulfur deficiency in field grown crops as yet does not appear to be a problem in Iowa soils, compared with some of the soils in Nebraska, North Dakota, Minnesota and Wisconsin. Responses of crops to sulfur in these states adjoining Iowa are confined, as a rule to well-drained, light-textured soils low in organic matter (Beaton, 1969). Freedom from sulfur deficiency in Iowa soils is probably a consequence of there being a predominance of fine-textured soils. However, some field experiments conducted in the 1920's by Erdman and Bollen (1925) indicated increased yields of alfalfa and oats and clover when gypsum was applied to fine sand, sandy loam, silt loam and loam soils.

Since the 1920's crop yields have more than doubled, thereby increasing the demand for nutrients. Furthermore, ordinary superphosphate, which provided sulfur for crops, has been replaced with double superphosphate, which does not contain any sulfur. Atmospheric sources of sulfur may decline markedly in the future with the introduction of air pollution control schemes. Thus, sulfur could become limiting on many Iowa soils which in the past appear to have been well supplied.

Before undertaking extensive field experiments with sulfur fertilizers, and before recommendations can be made as to which soils are likely to require additional sulfur,

laboratory, greenhouse and field-sampling studies should be undertaken to characterize the sulfur that is present in terms of amount and availability in representative soils. The research described in this dissertation was concerned with characterizing that fraction of sulfur that was available to plants, in some Iowa soils.

Sulfate sulfur was extracted with 0.1 M LiCl, $Ca(H_2PO_4)_2$ solution containing 500 ppm P, and with 0.5 M $NaHCO_3$ from a group of soils, representative of seven of the nine soil association areas in Iowa, and providing a wide range in texture, organic matter content and pH. Over all soils LiCl extracted as much sulfate sulfur as $Ca(H_2PO_4)_2$, with values ranging from 2 to 16 ppm. Only in the Weller subsoil, was there appreciably more sulfate sulfur extracted by $Ca(H_2PO_4)_2$ compared with LiCl. The additional 4-5 ppm of sulfate sulfur extracted by the phosphate solution was probably adsorbed sulfate.

In general, one must conclude that the soils used in this study contain little or no adsorbed sulfate. Fox et al. (1964b) likewise, found very little adsorbed sulfate in Nebraska soils when they compared the sulfate sulfur extracted by water to that extracted with $Ca(H_2PO_4)_2$. However, they worked mainly with coarse-textured soils which contained low levels of extractable sulfur and these soils are therefore not strictly comparable to Iowa soils.

The capacity of soils to adsorb sulfate is known to be dependent on a low pH in association with hydrous oxides of iron and aluminum, and 1:1 clays (Ensminger, 1954; Kamprath et al., 1956; and Chao et al., 1962b). As a rule very little sulfate sulfur is retained in the adsorbed form in soils above pH 6.0 (Reisenauer, 1967). Because all soils used in this study, with the exception of Weller, had pH values greater than 6.0 and eight of them had pH values higher than 7.0, it is not surprising that sulfate sulfur did not occur to any extent in the adsorbed form.

In this study $NaHCO_3$ extracted about three times as much sulfate sulfur as did LiCl or $Ca(H_2PO_4)_2$. However, compared with these extractants the amount of sulfate sulfur extracted by $NaHCO_3$ showed little relationship to sulfur taken up by plants in the greenhouse experiment. The use of 0.5 M $NaHCO_3$ for extraction of sulfate sulfur was first suggested by Kilmer and Nearpass (1960) who found that the sulfate sulfur extracted from soils of the southeastern United States was highly correlated with "A" values from a greenhouse study. Likewise Bardsley and Kilmer (1963) and Williams and Steinbergs (1964) obtained good correlation between sulfate sulfur extracted by $NaHCO_3$ and plant uptake. The data of Bardsley and Kilmer (1960) and Williams and Steinbergs (1964), however, shows that $NaHCO_3$ extracted appreciable amounts of adsorbed sulfate which

formed the greater part of the sulfur extracted. In the present study, and also that of Arkley (1961) who found no correlation between $NaHCO_3$ extractable sulfate and sulfur taken up by tomato plants, the sulfate sulfur present was low and occurred mainly in the water soluble form. Clearly, much of the sulfur extracted by $NaHCO_3$ from these soils must be in the form of organic sulfur compounds which are not readily available to plants.

The greenhouse experiment, 1/68, provided plant indices for the evaluation of the sulfate sulfur values obtained with laboratory extractants. From correlations made between dry matter yield, percent sulfur in ryegrass and yield of sulfur in ryegrass grown on soils to which no sulfur had been added and sulfur extracted by the three extractants, it was found that yield of sulfur in either harvests 1-3 or harvests 1-5 provided the best plant index of available sulfur. Because dry matter yields in harvests 1-3 and 1-5 were very highly correlated with yield of sulfur in ryegrass ($r = .92$ and $.95$), dry matter yields also provide useful indices of the available sulfur status.

The sulfate sulfur extracted by 0.1 M LiCl from air-dry soils at a soil to extractant ratio of 1:10 gave the highest correlations with yield of sulfur in ryegrass for harvests 1-3 and 1-5 and with the other plant indices. In general, yields of sulfur in ryegrass that had not

received applied sulfur were less well correlated with sulfate extracted by the $Ca(H_2PO_4)_2$ solution than they were with sulfate sulfur extracted with LiCl.

Correlations between sulfate extracted by LiCl and $Ca(H_2PO_4)_2$ and "a" values were not as high as those between sulfate sulfur extracted and yield of S or of dry matter in ryegrass. "a" values were calculated by extrapolation of the yield of sulfur regression line for each soil to the X axis according to the method of Dean (1954). The "a" value represents the amount of available sulfur in the soil in terms of the fertilizer standard added. Linear regression lines were fitted for each soil and although the r^2 value after removing the variance due to blocks was greater than 0.96 in most cases, three soils, Monona surface soil, and Weller surface and subsoil, which were well supplied with available sulfur, had r^2 values less than 0.90. The use of the whole regression line for the calculation of "a" values would appear to have given an index of plant available sulfur that is inferior to the index provided by the yield of sulfur in ryegrass that did not receive applied sulfur.

Air-drying of soils is known to result in increases in the "available" nutrient status. In particular air-drying has been shown to increase both the aerobic NO_3-N and anaerobic NH_4-N content of soils on incubation (Hanway and Ozus, 1966) and to increase the exchangeable potassium

content of both surface and subsoils (Hanway and Scott, 1959). Studies by Freney (1958), Barrow (1961) and Williams (1967b) have shown that air-drying increases the sulfate sulfur extracted from soils, and that much of the sulfur released by drying was plant available. In this study, air-drying of soils, besides increasing the level of anaerobic NH_4-N and exchangeable potassium, resulted in an increase in the amount of sulfate sulfur extracted. For LiCl and $Ca(H_2PO_4)_2$ extractions the increase in sulfate sulfur with drying averaged between 1-2 ppms. This increase in sulfate sulfur with drying was of a similar order to that reported by Barrow (1961), Williams and Steinbergs (1964) and Williams (1967b) who extracted air-dry soils with 0.15 per-cent $CaCl_2$.

A greenhouse experiment, designed to examine the effect of air-drying on sulfur availability, showed that air-drying prior to cropping significantly increased sulfur uptake by ryegrass. The effect was more marked at the lower levels of applied sulfur and where no sulfur had been applied.

Regression of sulfate sulfur extracted from field moist and air-dry soils and sulfur taken up from untreated soils by ryegrass, (Experiment 1/68), showed that a larger amount of the sulfate sulfur extracted was unavailable to plants on air-dry than on field moist soils. Further evidence for this was obtained when untreated soils were extracted

with 0.1 M LiCl after five crops of ryegrass had been harvested. On soils undried prior to extraction an average of 0.6 ppm of sulfate sulfur was extracted with LiCl, compared with 2.9 ppm in soils that had been air-dried. In the Webster and Fayette subsoils, where ryegrass had died because of severe sulfur deficiency, no more than 0.2 ppm sulfur could be extracted from the undried soils. However, the same soils air-dried prior to extraction, showed an average of 2.7 and 1.2 ppm S for the Webster and Fayette subsoils, respectively. Similar amounts of extractable sulfate sulfur have been found in soils after cropping, where plants were very deficient in sulfur (McClung et al., 1959; and Freney and Spenser, 1960). This unavailable sulfate, extractable after air-drying, is probably organic sulfate which would be reduced to sulfide along with inorganic sulfate in the Johnson Nishita digestion-distillation apparatus.

In spite of the fact that LiCl and $Ca(H_2PO_4)_2$ extract from air-dry soils more sulfate sulfur that is not readily available to plants, correlations between sulfur taken up by plants in the absence of applied sulfur and sulfate-sulfur extracted by LiCl or $Ca(H_2PO_4)_2$ were higher where soils had been air-dried prior to extraction. A possible explanation for the better relationship between the sulfate sulfur extractable after drying and plant uptake

of S is that air-drying releases to the extractant, some organic sulfate, which over a period of time would be mineralized to available inorganic sulfate. An estimate of the amount of sulfur taken up by plants, that came from mineralization of organic S, showed an average of 3.8 ppm S over all soils, compared with 4.6 ppm S that came from sulfate sulfur that was present initially as water soluble sulfate. Hence, any correlation which relates inorganic sulfur immediately available to the plants plus that fraction of the organic sulfur which can be mineralized in the presence of plants is likely to be better than one which does not take into account mineralizable sulfur. On the other hand, in soils where adsorbed sulfate is of little importance, the amount of water soluble sulfate sulfur present in soils prior to cropping may be highly correlated with the ability of the soil to mineralize sulfate. In this study the correlation coefficient was 0.693, which was highly significant. The regression equation was $Y = 1.48X - 2.99$, where Y = mg S/kg soil in ryegrass from five harvests estimated to be derived from mineralization, and X = the ppm of sulfate sulfur extracted by 0.1 M LiCl from undried soil prior to cropping. This equation implies that no mineralization of sulfur will occur when LiCl extractable sulfur from undried soils falls to about 2 ppm. Moreover, at values of LiCl extractable sulfate sulfur

less than 2 ppm, applied sulfate may even be immobilized.

Sulfur applied as gypsum to both surface soils and subsoils in the greenhouse, Experiment 1/68, was readily available to ryegrass. The recovery of applied sulfur over five harvests averaged 82 percent over all soils and with the exception of two extreme values ranged from 72 to 93 percent. The Weller subsoil in contrast to most other soils contained adequate available sulfate for five harvests of ryegrass. Consequently, a much smaller proportion (39 percent) of the applied sulfur was taken up by ryegrass from this soil.

With the exception of the Weller subsoil, the mean recovery of applied sulfate was of a similar order for both surface soils and subsoils. Although measurements were not made, it is likely that the remaining stubble and roots of the ryegrass plants would account for the greater part of sulfur that was not recovered in five harvests.

Greenhouse studies are indispensible for the evaluation of laboratory indices of available sulfur and provide useful information on the sulfur supplying capacity of various soil horizons and on the relative response to applied sulfur of crops grown on these soils under greenhouse conditions. Greenhouse studies cannot, however, be used to predict the response of field-grown crops to applied sulfur. As outlined earlier in the review of literature,

the supply of available sulfur in the soil, and hence the response to applied sulfur, is affected by many factors such as the supply of sulfur from the atmosphere, the contribution of available sulfate from the subsoil, and the degree to which the soil adsorbs sulfate, which in turn helps the soil retain sulfate against leaching.

In order to obtain information as to the supply of sulfur in some Iowa soils, that would be available to crop plants during the growing season, samples were taken in one foot increments to a depth of four feet at six sites at the start, the middle and at the end of the growing season. Water soluble sulfate extracted with 0.1 M LiCl on dried samples, at a 1:5 soil to extractant ratio, was used to characterize the available sulfur status of the samples. Earlier it was shown that the sulfate sulfur extracted with LiCl from air-dry samples correlated best with sulfur taken up by ryegrass in the greenhouse. This study showed that the sulfate sulfur content of surface soils was similar for fine-textured soils, markedly lower for Hagener loamy sand, and that values averaged over the growing season ranged from 2.0 to 6.4 ppm. In most of the soils sampled, the sulfate sulfur content was reasonably uniform with depth, whereas in the well-drained Sharpsburg and Fayette soils, the sulfate content declined consistently down the profile. Roberts and Koehler (1968), in eastern Washington

soils found that LiCl extractable sulfur, although lower than that found in these Iowa soils, was also reasonably uniform with depth. The lack of any marked increase with depth in extractable sulfate sulfur was an indication that adsorbed sulfate, or sulfate sulfur precipitated in a caliche-like layer, was not present.

Between May and November the average sulfate sulfur content of the soil decreased by 1.34 ppm, a drop which over the four foot depth of soil amounts to 21 lb. of sulfur per acre. This decrease of sulfate sulfur, over the growing season represents the resultant of several processes which are operating simultaneously, viz., plant uptake and leaching of sulfate, possibly gaseous loss of H_2S and mercaptans during wet periods when oxygen tensions are low, mineralization of organic sulfur and accessions of sulfur, mainly as SO_2, from the atmosphere. No attempt was made to assess the contribution of each of these processes, but it is considered that the magnitude of each would tend to vary from soil to soil. The Hagener soil, of particular interest because it was fallowed during the growing season, decreased by 0.7 ppm or 11 lb. per acre of sulfate sulfur over the four foot depth. On the other hand Clarion and Webster soils, both planted to corn decreased by 2.2 ppm or 35 lb. per acre of sulfate sulfur.

Presumably between November and the following May,

gains in sulfate would exceed losses and there would again be a level of sulfate sulfur present within the root zone, comparable to that present in May, 1969. While the estimate made of levels of available sulfate sulfur in the root zone exceeded by a factor of 3 the sulfur requirement of 100 bushel per acre corn crop, it cannot as yet be determined with our present state of knowledge whether sulfate sulfur levels are being maintained at the expense of the organic sulfur reserves in the soil.

It is possible that much of a crop's sulfur requirements are met from sulfur supplied by the atmosphere. The present evidence would suggest that considerably more sulfur is received from the atmosphere than is utilized by crops. Recent analyses of tile drainage and surface runoff water from Iowa corn fields indicate between 10 and 20 ppm sulfate sulfur present. This may possibly represent the sulfur from the atmosphere plus sulfur mineralized less the amount used by the crop and that remaining in soil in water soluble form. If the reserves of sulfur in the soil are not being depleted then the contribution from the atmosphere is probably greater than was once believed.

Unfortunately there is no recent data available for rural Iowa. Erdman and Bollen (1925) recorded an average of 15 lbs. of sulfur per acre per year in the rainfall collected two miles south of Ames. Because of the proximity

to an urban area this value may be higher than that of more remote rural areas. Recent values for rural eastern Nebraska (Fox et al., 1964a) and north central Minnesota (Seim et al., 1969) average about 6 lb. of sulfur per acre per year. Presumably sulfur in rainfall in rural Iowa would lie between 6 and 15 lb. per acre per year.

Apparently sulfur which can be adsorbed directly from the air by soil, and to a lesser degree by plants, may be of greater magnitude than that brought down in rainfall (Johansson, 1959). Recent studies by Seim and Caldwell (1970) indicate considerable adsorption of SO_2 by soils both wet and dry, which could be recovered to a large degree from the soil as sulfate. Until such time as studies have been carried out to determine the atmospheric contribution, both adsorbed directly by soil and that entering the soil in precipitation, we can only speculate as to whether the crop needs and the sulfur reserves in the soil are being maintained by atmospheric sources.

Sandy soils appear to have lower levels of extractable sulfate than do the finer-textured soils. Within any given area the atmospheric supply will tend to be uniform from one soil to another. However, coarse-textured soils because of their lower specific surface, may absorb less sulfur directly than would fine-textured soils. Moreover, because of their lower water-holding capacity there would

be a tendency toward more drainage water moving through them and hence more leaching of sulfate sulfur.

SUMMARY AND CONCLUSIONS

The objectives of the study were to determine a suitable index of available sulfur in some representative Iowa soils, to determine the availability of applied sulfate under greenhouse conditions, to assess the effects of air-drying on the availability of sulfur, and to examine the distribution of available sulfur with depth and time in some representative soils.

Sixteen surface soils and 5 subsoils (18-24 in), with five rates of applied sulfur as gypsum, were cropped through five harvests with annual ryegrass in the greenhouse. Yields of sulfur in the ryegrass from soil that had not been treated with gypsum were used as the "best" plant index of available sulfur with which to correlate laboratory indices of extractable sulfur. The regression of yield of sulfur taken up in ryegrass on sulfur applied to each soil was used to calculate "a" values as a further index of available sulfur.

In the laboratory, sulfate sulfur was extracted from both field moist and air-dry soils, with 0.1 M LiCl, $Ca(H_2PO_4)_2$ solution containing 500 ppm P, and 0.5 M $NaHCO_3$ at soil to extractant ratios of 1:5 and 1:10. Yield of sulfur in ryegrass from five cuttings was highly correlated with sulfate sulfur extracted with 0.1 M LiCl from air-dry soil at a ratio of 1:10 ($r = 0.874$). Sulfate

sulfur extracted by the $Ca(H_2PO_4)_2$ solution did not differ significantly with that extracted by 0.1 M LiCl, but correlations with plant uptake of sulfur were lower than those obtained with LiCl. $NaHCO_3$ extracted about three times as much sulfate sulfur as did LiCl or $Ca(H_2PO_4)_2$, but the amount extracted was not significantly correlated with sulfur uptake by plants. The relationships between "a" values and sulfate sulfur extracted by LiCl and $Ca(H_2PO_4)_2$, were not as good as those relationships obtained using yield of sulfur in ryegrass from soils which had not received added sulfur.

The surface soils used in this study contained an average of 250 ppm total sulfur which ranged from 68 to 452 ppm S, whereas subsoils averaged 140 ppm total S with a range of 85 to 210 ppm. Of the total sulfur present in surface soils, an average of 54 percent was HI-reducible sulfur, 8 percent was carbon-bonded sulfur and 2.6 percent was sulfate sulfur extractable with LiCl. Of the total sulfur present in subsoils an average of 72 percent was HI-reducible sulfur, 4 percent was carbon-bonded sulfur and 5.0 percent was sulfate sulfur extractable with LiCl.

The sulfate sulfur extracted with LiCl and $Ca(H_2PO_4)_2$ averaged 6.2 ppm S (range 2.2 - 10.4) in surface soils and 7.6 ppm S (range 5.1 - 15.6) in subsoils. Because $Ca(H_2PO_4)_2$ extracted no more sulfate sulfur from soils

and subsoils than did LiCl with the exception of the Weller subsoil, it is concluded that the Iowa soils studied did not contain significant amounts of adsorbed sulfate. Water soluble sulfate sulfur extracted by LiCl appears to be readily available, according to greenhouse tests. After a period of cropping in the greenhouse, sulfate sulfur on undried soils was found to have been reduced to an average of 0.6 ppm S. The sulfur taken up by the ryegrass plants in most cases exceeded the reduction in the level of sulfate sulfur extractable with 0.1 M LiCl. The additional sulfur taken up by ryegrass gave an estimate of the mineralization of some fraction of the organic sulfur. Over all soils cropping reduced the sulfate sulfur level by 4.6 ppm S and removed a further 3.8 ppm S, estimated to be derived from mineralization of organic sulfur.

Greenhouse observations suggested, and subsequent analyses confirmed, that surface soils, even when depleted of extractable sulfate sulfur, will continue to support a very limited plant growth because of a small but continuous supply of sulfate mineralized from organic matter. The Clarion, Webster and Fayette subsoils, however, once depleted of sulfate sulfur would not support plant growth, presumably because of lack of mineralization of organic sulfur.

In the greenhouse experiment, ryegrass on half of the

soils responded significantly to applied sulfur at the first harvest. On most of the responsive soils, the percent sulfur at first harvest was less than the critical level of 0.25 percent S. Applied sulfur was readily available to plants; over three harvests the mean recovery was 66 percent, while over five harvests mean recovery was 82 percent. The low percent recovery on the Weller subsoil (39 percent) differed significantly from all other values, and was a consequence of this subsoil having an adequate supply of available sulfate.

Air-drying was found to increase the amount of sulfate sulfur extracted by all three extractants. With LiCl and $Ca(H_2PO_4)_2$, the increase in sulfate extracted amounted to 1-2 ppm S. The effect of air-drying soils prior to cropping was shown, in the greenhouse experiment, to increase the uptake of sulfur by ryegrass. On the other hand while air-drying appeared to increase the amount of sulfate extracted it also appeared to release some sulfate which was unavailable to plants.

A time and depth of sampling study showed that the top four feet of the coarse-textured Hagener loamy sand contained markedly less sulfate sulfur than did the other fine-textured soils sampled. An estimate of the available sulfur content of some fine-textured soils over the growing season indicated an average of 74 lb. of sulfate sulfur

present in the top four feet compared with 31 lb. in a Hagener loamy sand. Between May and November there was an average decrease of 1.3 ppm or 21 lb. of sulfate sulfur in the top four feet of soil. Such a decrease indicates that removal processes, such as plant uptake and leaching during the growing season, outweigh the processes of atmospheric addition and mineralization of organic sulfur.

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APPENDIX

Table 36. Harvest dates and nutrients added to pots in greenhouse experiments.

Crop	Cropping dates start to harvest	No. of growing days	Nutrients added (mg/pot) N	P	K	S
		Experiment 1/68				
Sand culture	Aug. 5 to Sept. 16	42	88.2	10.5	95.0	0.5
1	Sept. 16 to Oct. 17	31	100.8	12.0	108.8	
2	Oct. 17 to Nov. 25	39	126.0	15.5	136.4	
3	Nov. 25 to Jan. 8	44	126.0	15.5	136.4	
4	Jan. 8 to Feb. 27	50	164.0	20.4	177.4	
5	Feb. 27 to April 6	38	126.0	15.5	136.4	
Total		243	731.0	89.4	790.4	0.5
		Experiment 2/68				
Sand culture	Nov. 7 to Dec. 16	39	63.0	7.5	68.0	0.5
1	Dec. 16 to Jan. 24	39	126.0	15.5	136.4	
2	Jan. 24 to Feb. 27	34	163.8	20.2	177.4	
3	Feb. 27 to April 5	37	163.8	20.2	177.4	
Total		149	516.6	63.4	559.2	0.5

Table 37. Some physical characteristics of soils used in experiments

Soil type	Lab. no.	Mechanical analyses: sand > 50 μ	silt 2-50 μ	clay < 2 μ	H_2O held at tension: 1/3 bar	15 bar	H_2O present at collection of bulk sample
		percent					
Surface soils							
Clarion l	1	42.3	36.5	21.2	21.7	10.5	16.0
Webster cl	2	25.7	41.6	32.7	30.1	18.4	17.0
Hagener ls	3	79.4	13.8	6.8	5.8	2.8	5.3
Hamburg sil	4	7.7	76.0	16.3	25.3	10.4	12.3
Ida sil	5	5.3	71.7	23.0	28.6	12.3	10.1
Monona sil	6	2.6	70.9	26.5	25.7	11.6	21.1
Marshall sicl	7	1.5	64.0	34.5	28.4	14.3	14.3
Sharpsburg sicl	8	1.5	62.4	36.1	29.5	15.9	17.4
Grundy sicl	9	3.2	62.7	34.1	29.1	13.8	21.7
Albaton sicl	10	5.8	58.3	35.9	31.5	15.7	16.8
Sarpy l	11	44.6	43.0	12.4	14.7	6.5	10.7
Tama sil	12	2.3	72.3	25.4	29.1	11.3	11.6

Table 37. (Continued)

Soil type	Lab. no.	Mechanical analyses: sand > 50 μ	silt 2-50 μ	clay < 2 μ	H_2O held at tension: 1/3 bar	15 bar	H_2O present at collection of bulk sample
		percent					
Fayette sil	13	11.1	65.2	23.7	21.9	11.1	20.6
Weller sil	14	4.5	74.2	21.3	24.7	8.9	13.9
Thurman s	15	86.0	7.7	6.3	4.6	2.6	1.5
Dorset sl	16	70.8	20.5	8.7	13.3	5.5	2.0
			Subsoils				
Clarion scl	17	13.9	25.2	20.9	15.4	8.6	14.6
Webster l	18	39.0	34.2	26.8	23.3	13.0	9.3
Monona sil	19	3.0	72.8	23.9	25.7	11.8	13.8
Fayette sil	20	7.2	69.4	23.4	22.3	11.7	20.2
Weller sic	21	2.2	57.7	40.1	32.0	18.9	21.2

Table 38. Some chemical characteristics of soils used in experiments

Soil type	Lab. no.	Organic C %	$CaCO_3$ %	pH
		Surface soils		
Clarion l	1	2.10	0.0	6.1
Webster cl	2	2.80	0.0	6.3
Hagener ls	3	0.46	0.23	6.9
Hamburg sil	4	0.91	9.55	8.3
Ida sil	5	1.01	0.46	7.9
Monona sil	6	1.51	0.00	7.0
Marshall sicl	7	1.52	0.00	7.5
Sharpsburg sicl	8	1.57	0.00	7.1
Grundy sicl	9	2.30	0.00	6.5
Albaton sicl	10	1.33	2.96	7.8
Sarpy l	11	0.77	5.00	8.2
Tama sil	12	1.88	0.00	6.5
Fayette sil	13	1.19	0.00	6.4
Weller sil	14	1.32	0.00	5.2
Thurman s	15	0.11	0.45	7.1
Dorset sl	16	1.62	0.00	6.6

[a] NH_4-N + NO_3-N in soil at time of collection.

Anaerobic NH_4-N	Initial NO_3-N	Available N[a]	Available P	Exch. K
		ppm		
		Surface soils		
18	40	56	13	67
67	32	45	19	78
9	24	36	28	82
98	13	23	7	150
105	46	56	14	368
30	93	103	56	271
57	97	107	33	284
31	68	79	14	166
31	50	62	28	162
26	159	169	98	> 1000
73	33	42	14	321
33	54	68	47	203
34	48	59	23	130
26	189	235	19	92
6	33	74	44	74
48	22	37	38	82

Table 38. (Continued)

Soil type	Lab. no.	Organic C %	$CaCO_3$ %	pH
		Subsoils		
Clarion scl	17	0.56	1.14	6.6
Webster l	18	0.51	4.32	8.3
Monona sil	19	0.36	0.68	6.8
Fayette sil	20	0.18	0.00	5.7
Weller sic	21	0.38	0.00	5.2

Anaerobic NH_4-H	Initial NO_3-N	Available N[a]	Available P	Exch. K
		ppm		
		Subsoils		
2	27	38	9	22
4	14	24	11	39
3	36	46	11	47
3	36	46	46	28
6	12	25	18	43

Table 39. Sulfate sulfur extracted from 21 soils with three extractants of two ratios of soil to extractant on field moist (FM) and air-dry (AD) samples

Soil	Extractable SO_4-S (ppm)											
	LiCl (0.1 M)				$Ca(H_2PO_4)_2$ (500 ppm P)				$NaHCO_3$ (0.5 M)			
	1:5		1:10		1:5		1:10		1:5		1:10	
	FM	AD	FM	AD	FM	AD	FM	AD	FM	AD	FM	AD
					Surface soils							
Hamburg	2.0	4.7	2.5	6.1	1.6	3.9	1.9	4.4	9.1	12.3	10.5	13.6
Hagener	1.6	3.2	3.0	3.7	2.0	2.6	2.9	3.3	12.1	12.1	11.3	14.0
Webster	3.2	5.5	4.7	6.2	4.9	5.9	4.3	6.5	18.4	20.4	20.5	22.7
Thurman	3.3	3.5	3.6	4.2	1.3	2.7	1.9	3.1	7.1	8.0	9.1	9.2
Dorset	5.3	5.5	5.6	7.2	4.7	4.7	5.6	5.8	17.9	17.6	17.0	14.1
Sharpsburg	4.0	5.8	4.4	5.6	4.9	6.8	5.0	8.1	25.5	34.7	36.6	39.1
Fayette	3.6	4.7	3.2	5.9	4.6	7.2	4.3	6.6	25.5	29.1	28.8	38.0
Clarion	4.6	6.7	4.8	9.4	5.7	7.7	7.1	10.7	37.8	42.4	35.8	41.1
Sarpy	3.4	7.1	5.7	7.9	4.6	6.9	5.6	7.4	30.4	31.1	32.7	34.3
Marshall	7.4	8.8	8.8	10.5	8.1	9.0	9.9	10.5	29.2	31.9	32.3	35.5
Grundy	5.7	8.8	7.8	9.6	5.3	7.8	5.6	9.2	28.8	36.3	37.4	43.2

Table 39. (Continued)

Soil	Extractable SO_4-S (ppm)											
	LiCl (0.1 M)				$Ca(H_2PO_4)_2$ (500 ppm P)				$NaHCO_3$ (0.5 M)			
	1:5		1:10		1:5		1:10		1:5		1:10	
	FM	AD	FM	AD	FM	AD	FM	AD	FM	AD	FM	AD
Albaton	7.9	8.4	9.4	9.6	8.3	8.4	9.2	9.9	12.1	12.4	14.5	16.1
Ida	7.4	8.0	8.3	9.3	5.5	7.8	5.5	7.8	15.4	15.6	17.1	16.6
Weller	5.8	8.9	8.3	11.4	3.8	6.3	4.8	7.6	25.7	26.1	28.6	28.8
Monona	7.9	11.1	8.6	13.8	8.0	12.4	8.7	12.6	25.5	33.1	31.5	37.1
Subsoils												
Clarion	5.5	6.2	4.0	5.9	5.9	8.9	6.7	8.6	27.2	36.1	34.8	33.2
Webster	5.9	6.6	5.8	6.4	5.7	4.4	6.3	7.0	8.6	9.3	8.3	8.3
Fayette	4.1	4.1	4.7	6.4	5.6	5.3	6.4	8.8	12.4	12.9	14.4	13.8
Monona	5.0	5.7	6.3	8.2	4.2	5.1	4.8	6.2	14.9	20.7	18.9	21.7
Weller	10.4	11.7	12.8	13.8	14.1	15.8	15.0	17.8	29.2	33.7	29.9	31.7

Table 40. Chemical and plant indices used in the correlation matrix given in Table 41

Index no.	Description of index
1	LiCl extractable sulfate, ppm S, FM soil, 1:5
2	" " " " AD soil, 1:5
3	" " " " FM soil, 1:10
4	" " " " AD soil, 1:10
5	$Ca(H_2PO_4)_2$ " " " FM soil, 1:5
6	" " " " AD soil, 1:5
7	" " " " FM soil, 1:10
8	" " " " AD soil, 1:10
9	$NaHCO_3$ " " " FM soil, 1:5
10	" " " " AD soil, 1:5
11	" " " " FM soil, 1:10
12	" " " " AD soil, 1:10
13	Total S in soil, ppm S
14	HI-reducible S, "
15	Carbon-bonded S, "
16	Organic carbon, percent C
17	Dry matter yield of ryegrass, harvest 1, g/pot
18	Percent sulfur in ryegrass, " % S
19	Sulfur yield in ryegrass, " mg/pot
20	Dry matter yield of ryegrass, harvests 1-3, g/pot

Table 40. (Continued)

Index no.	Description of index
21	Percent sulfur in ryegrass, harvests 1-3, % S
22	Sulfur yield in ryegrass, " mg/pot
23	Dry matter yield of ryegrass, harvests 1-5, g/pot
24	Percent sulfur in ryegrass, " % S
25	Sulfur yield in ryegrass, " mg/pot
26	"a" value, " ppm S

Table 41. Correlation matrix showing relationships among both chemical and plant indices, of extractable sulfur in soils

	1	2	3	4	5	6
1	1.00					
2	.90	1.00				
3	.94	.91	1.00			
4	.85	.95	.89	1.00		
5	.88	.79	.83	.75	1.00	
6	.84	.86	.77	.82	.91	1.00
7	.88	.78	.83	.76	.98	.88
8	.84	.85	.80	.83	.94	.95
9	.38	.56	.35	.54	.45	.63
10	.36	.55	.30	.51	.44	.65
11	.36	.55	.32	.49	.41	.62
12	.30	.52	.27	.48	.37	.60
13	.29	.43	.31	.41	.23	.33
14	.31	.47	.32	.46	.28	.41
15	.03	.27	.08	.22	.08	.25
16	- .09	.18	- .03	.14	- .06	.04
17	.44	.55	.50	.57	.20	.31
18	.78	.67	.73	.69	.63	.63
19	.72	.76	.72	.80	.47	.58
20	.74	.81	.81	.84	.60	.72

7	8	9	10	11	12	13
1.00						
.93	1.00					
.47	.62	1.00				
.44	.62	.97	1.00			
.40	.59	.96	.98	1.00		
.36	.56	.94	.97	.98	1.00	
.20	.26	.26	.27	.30	.35	1.00
.25	.35	.36	.40	.42	.46	.95
.02	.14	.44	.45	.51	.59	.80
- .09	.01	.33	.30	.32	.35	.73
.21	.28	.36	.33	.42	.40	.38
.63	.65	.13	.15	.15	.09	- .07
.48	.55	.26	.26	.30	.27	.15
.59	.65	.39	.37	.41	.41	.41

Table 41. (Continued)

	14	15	16	17	18	19
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14	1.00					
15	.74	1.00				
16	.67	.80	1.00			
17	.30	.45	.23	1.00		
18	.00	- .31	-.45	.29	1.00	
19	.18	.03	-.17	.71	.85	1.00
20	.38	.34	.08	.75	.61	.81

20	21	22	23	24	25	26

1.00

Table 41. (Continued)

	1	2	3	4	5	6
21	.75	.68	.76	.74	.73	.73
22	.81	.83	.84	.87	.70	.78
23	.77	.82	.83	.84	.70	.79
24	.62	.56	.65	.66	.66	.64
25	.81	.84	.85	.87	.73	.81
26	.74	.72	.79	.74	.79	.81

7	8	9	10	11	12	13
.71	.74	.26	.24	.20	.17	- .08
.69	.75	.32	.32	.31	.30	.15
.67	.71	.36	.34	.36	.36	.40
.64	.70	.22	.20	.16	.14	- .12
.71	.76	.32	.32	.31	.30	.21
.76	.79	.29	.28	.25	.22	- .01

Table 41. (Continued)

	14	15	16	17	18	19
21	- .04	- .22	- .36	.29	.87	.74
22	.17	.02	- .18	.54	.84	.88
23	.35	.31	.08	.60	.60	.73
24	- .07	- .24	- .37	.23	.82	.67
25	.21	.08	- .12	.51	.72	.83
26	.03	- .13	- .24	.22	.71	.59

20	21	22	23	24	25	26
.74	1.00					
.91	.92	1.00				
.96	.77	.91	1.00			
.62	.95	.82	.65	1.00		
.92	.91	.99	.95	.81	1.00	
.74	.90	.88	.83	.80	.90	1.00

Table 42. Dry matter yields, percent sulfur and yield of sulfur in ryegrass, by soils, harvests and sulfur treatments, in Experiment 1/68 (soils arranged in order of increasing sulfur uptake, by ryegrass not treated with added sulfur)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Hamburg	4	1	0	1.41	.147	2.05
			7.5	2.25	.351	7.90
			15	2.56	.426	10.92
			22.5	2.49	.449	11.22
			30	2.32	.443	10.26
		2	0	0.74	.095	0.71
			7.5	2.72	.145	3.93
			15	3.86	.193	7.46
			22.5	3.69	.310	11.47
			30	3.49	.311	10.88
		3	0	0.28	.042	0.12
			7.5	1.12	.125	1.39
			15	2.28	.110	2.54
			22.5	4.12	.158	6.49
			30	4.38	.212	9.15
		4	0	0.32	.174	0.54
			7.5	0.69	.142	0.98
			15	0.89	.142	1.27
			22.5	2.11	.150	3.16
			30	3.48	.170	5.85
		5	0	0.50	.065	0.32
			7.5	0.66	.104	0.70
			15	0.56	.096	0.54
			22.5	0.97	.122	1.18
			30	2.00	.091	1.82
Hagener	3	1	0	1.59	.163	2.59
			7.5	2.37	.376	8.94
			15	2.08	.518	10.78
			22.5	2.08	.568	11.83
			30	2.18	.574	12.50

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Hagener (cont)	3	2	0	0.80	.172	1.37
			7.5	1.87	.137	2.58
			15	3.48	.212	7.39
			22.5	3.46	.356	12.34
			30	3.35	.501	16.90
		3	0	0.46	.104	0.48
			7.5	0.89	.131	1.16
			15	1.97	.110	2.20
			22.5	3.27	.125	4.09
			30	3.60	.213	7.68
		4	0	0.43	.188	0.82
			7.5	0.65	.173	1.13
			15	0.81	.153	1.25
			22.5	1.56	.173	2.70
			30	1.77	.164	2.92
		5	0	0.49	.091	0.45
			7.5	0.68	.110	0.76
			15	0.58	.093	0.53
			22.5	0.91	.150	1.31
			30	1.07	.116	1.25
Webster	2	1	0	2.96	.144	4.28
			7.5	3.33	.281	9.37
			15	3.43	.394	13.52
			22.5	3.44	.448	15.40
			30	3.43	.427	14.64
		2	0	1.51	.131	1.98
			7.5	2.80	.159	4.47
			15	3.78	.259	9.80
			22.5	3.83	.305	11.61
			30	3.82	.358	13.63

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Webster (cont)	2	3	0	0.95	.189	1.82
			7.5	1.16	.146	1.67
			15	2.29	.168	3.88
			22.5	3.74	.183	6.74
			30	3.87	.221	8.41
		4	0	0.90	.185	1.77
			7.5	0.96	.124	1.19
			15	1.33	.127	1.69
			22.5	2.15	.217	4.71
			30	3.24	.121	3.89
		5	0	0.54	.118	0.64
			7.5	0.58	.103	0.61
			15	0.69	.097	0.67
			22.5	0.93	.118	1.10
			30	1.47	.110	1.62
Thurman	15	1	0	2.87	.294	8.46
			7.5	3.05	.445	13.53
			15	3.14	.521	16.35
			22.5	2.98	.536	15.94
			30	2.94	.634	18.51
		2	0	1.79	.113	2.08
			7.5	3.07	.154	4.75
			15	3.54	.243	8.58
			22.5	3.72	.300	11.15
			30	3.69	.349	12.88
		3	0	0.42	.123	0.52
			7.5	0.90	.118	1.06
			15	2.11	.138	2.92
			22.5	3.14	.181	5.64
			30	3.64	.311	8.74

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Thurman (cont)	15	4	0	0.29	.183	0.52
			7.5	0.42	.159	0.66
			15	0.58	.145	0.83
			22.5	1.41	.132	1.85
			30	2.81	.157	4.46
		5	0	0.33	.056	0.19
			7.5	0.35	.046	0.16
			15	0.33	.059	0.20
			22.5	0.60	.108	0.65
			30	1.12	.103	1.10
Dorset	16	1	0	2.81	.275	7.74
			7.5	3.09	.441	13.61
			15	2.97	.567	16.85
			22.5	3.04	.558	16.97
			30	3.05	.608	18.56
		2	0	1.47	.103	1.52
			7.5	2.50	.128	3.21
			15	3.85	.272	10.46
			22.5	3.66	.393	14.33
			30	3.68	.414	15.15
		3	0	0.49	.160	0.79
			7.5	0.79	.156	1.23
			15	1.88	.144	2.71
			22.5	3.15	.217	6.84
			30	3.20	.354	11.30
		4	0	0.71	.132	0.94
			7.5	0.91	.153	1.39
			15	1.06	.141	1.50
			22.5	1.53	.147	2.24
			30	2.20	.171	3.76

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Dorset (cont)	16	5	0	0.76	.106	0.81
			7.5	0.86	.121	1.04
			15	0.88	.131	1.15
			22.5	1.21	.123	1.49
			30	1.48	.096	1.42
Sharpsburg	8	1	0	3.28	.177	5.81
			7.5	3.70	.393	14.53
			15	3.87	.429	16.63
			22.5	3.78	.482	18.21
			30	3.86	.456	17.60
		2	0	1.71	.107	1.83
			7.5	2.87	.140	4.03
			15	4.03	.210	8.48
			22.5	3.94	.275	10.80
			30	3.81	.314	11.92
		3	0	0.85	.105	0.89
			7.5	1.29	.100	1.25
			15	2.48	.115	2.84
			22.5	4.18	.163	6.74
			30	4.14	.231	9.17
		4	0	0.98	.140	1.37
			7.5	0.96	.137	1.31
			15	1.37	.123	1.69
			22.5	2.76	.132	3.65
			30	4.21	.199	8.48
		5	0	0.91	.095	0.86
			7.5	0.71	.099	0.71
			15	0.83	.126	1.04
			22.5	1.25	.091	1.12
			30	2.77	.106	3.02

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Fayette	13	1	0	2.98	.189	5.63
			7.5	3.32	.383	12.70
			15	3.34	.503	16.79
			22.5	3.22	.516	16.58
			30	3.39	.563	19.03
		2	0	1.89	.123	2.34
			7.5	2.77	.124	3.43
			15	3.85	.228	8.64
			22.5	3.99	.371	14.75
			30	3.92	.458	17.88
		3	0	0.91	.163	1.46
			7.5	1.18	.165	1.93
			15	2.11	.191	4.01
			22.5	3.79	.201	7.60
			30	4.01	.248	9.99
		4	0	0.77	.141	1.08
			7.5	0.90	.153	1.38
			15	0.99	.151	1.48
			22.5	1.69	.176	3.01
			30	2.66	.165	4.40
		5	0	0.78	.106	0.83
			7.5	0.88	.095	0.84
			15	0.82	.095	0.79
			22.5	1.09	.084	0.92
			30	1.42	.084	1.19
Clarion	1	1	0	2.69	.192	5.18
			7.5	2.95	.368	10.86
			15	3.06	.423	12.93
			22.5	2.97	.535	15.91
			30	3.20	.553	17.65

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Clarion (cont)	1	2	0	1.82	.140	2.55
			7.5	2.88	.163	4.67
			15	3.60	.263	9.45
			22.5	3.44	.391	13.50
			30	3.85	.453	17.43
		3	0	1.00	.221	2.15
			7.5	1.54	.129	2.03
			15	2.59	.177	4.58
			22.5	3.69	.191	6.97
			30	4.05	.237	9.62
		4	0	0.82	.193	1.58
			7.5	1.09	.170	1.88
			15	1.43	.140	2.01
			22.5	1.91	.137	2.59
			30	3.03	.147	4.49
		5	0	0.84	.118	0.96
			7.5	0.63	.120	0.74
			15	0.68	.120	0.84
			22.5	0.96	.110	1.05
			30	1.63	.116	1.90
Tama	12	1	0	2.77	.286	7.92
			7.5	3.13	.419	13.11
			15	3.19	.479	15.22
			22.5	3.09	.532	16.44
			30	3.32	.522	17.33
		2	0	1.87	.091	1.70
			7.5	3.31	.183	6.19
			15	3.99	.226	9.05
			22.5	3.81	.350	13.29
			30	3.96	.433	17.13

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Tama (cont)	12	3	0	1.30	.117	1.52
			7.5	1.60	.119	1.90
			15	2.86	.118	3.35
			22.5	4.13	.192	7.74
			30	4.41	.333	14.31
		4	0	0.95	.113	1.08
			7.5	1.08	.130	1.39
			15	1.50	.108	1.62
			22.5	2.37	.123	2.92
			30	3.72	.142	5.27
		5	0	0.79	.081	0.65
			7.5	0.83	.084	0.70
			15	0.95	.087	0.83
			22.5	1.30	.093	1.20
			30	1.98	.112	2.22
Sarpy	11	1	0	2.73	.186	5.07
			7.5	3.01	.380	11.39
			15	3.03	.425	12.87
			22.5	3.03	.491	14.87
			30	3.08	.423	13.04
		2	0	2.24	.144	3.24
			7.5	3.29	.218	7.18
			15	3.84	.249	9.58
			22.5	3.74	.386	14.51
			30	3.70	.472	17.43
		3	0	1.58	.155	2.42
			7.5	3.05	.139	4.29
			15	3.92	.155	6.08
			22.5	4.27	.215	9.24
			30	4.19	.206	8.59

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Sarpy (cont)	11	4	0	1.64	.147	2.41
			7.5	2.22	.181	3.94
			15	2.96	.148	4.39
			22.5	3.52	.151	5.31
			30	4.21	.184	7.73
		5	0	1.39	.108	1.49
			7.5	1.43	.120	1.71
			15	1.86	.087	1.62
			22.5	2.48	.111	2.78
			30	3.35	.092	3.10
Marshall	7	1	0	3.63	.253	9.21
			7.5	4.04	.394	15.92
			15	3.93	.408	15.69
			22.5	4.07	.432	17.59
			30	4.03	.489	19.72
		2	0	1.97	.091	1.79
			7.5	3.35	.133	4.45
			15	3.84	.208	8.02
			22.5	4.17	.291	12.11
			30	3.98	.376	14.98
		3	0	0.96	.098	0.94
			7.5	1.56	.119	1.86
			15	3.56	.124	4.39
			22.5	4.27	.187	7.95
			30	4.20	.219	9.18
		4	0	0.93	.103	0.95
			7.5	1.13	.123	1.39
			15	1.89	.132	2.51
			22.5	2.74	.129	3.56
			30	4.17	.181	7.54

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Marshall (cont)	7	5	0	0.87	.118	1.02
			7.5	0.72	.144	1.03
			15	1.03	.122	1.26
			22.5	1.19	.097	1.14
			30	2.05	.100	2.06
Grundy	9	1	0	3.31	.309	10.06
			7.5	3.32	.462	15.19
			15	3.44	.560	19.29
			22.5	3.48	.617	21.45
			30	3.57	.591	21.05
		2	0	2.53	.118	3.03
			7.5	3.35	.183	6.12
			15	3.79	.323	12.17
			22.5	3.67	.384	14.15
			30	3.98	.359	14.18
		3	0	1.31	.114	1.48
			7.5	1.94	.117	2.27
			15	3.27	.121	3.93
			22.5	4.17	.171	7.06
			30	4.22	.255	10.77
		4	0	1.30	.179	2.33
			7.5	1.34	.134	1.85
			15	2.01	.122	2.46
			22.5	2.66	.141	3.75
			30	3.99	.167	6.72
		5	0	0.95	.130	1.23
			7.5	0.95	.096	0.92
			15	1.22	.124	1.49
			22.5	1.45	.110	1.61
			30	2.22	.126	2.81

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Albaton	10	1	0	3.25	.304	9.86
			7.5	3.68	.308	11.46
			15	3.80	.404	15.32
			22.5	3.43	.510	17.33
			30	3.80	.548	20.65
		2	0	2.72	.157	4.29
			7.5	4.71	.274	12.93
			15	4.69	.333	15.61
			22.5	4.51	.376	16.97
			30	4.64	.352	16.32
		3	0	1.78	.089	1.60
			7.5	3.78	.126	4.75
			15	4.12	.180	7.41
			22.5	4.30	.210	8.98
			30	4.49	.236	10.58
		4	0	1.79	.152	2.78
			7.5	3.42	.132	4.45
			15	4.01	.201	8.06
			22.5	4.34	.220	9.59
			30	4.99	.238	11.93
		5	0	2.11	.104	2.19
			7.5	2.36	.116	2.73
			15	3.33	.120	3.97
			22.5	3.95	.122	4.83
			30	5.57	.154	8.56
Ida	5	1	0	3.07	.381	11.51
			7.5	3.12	.462	14.26
			15	3.13	.498	14.85
			22.5	3.41	.493	16.81
			30	3.50	.520	18.21

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Ida (cont)	5	2	0	2.89	.122	3.54
			7.5	3.93	.168	6.59
			15	4.12	.337	13.82
			22.5	4.15	.407	16.83
			30	4.13	.389	16.09
		3	0	1.47	.148	2.23
			7.5	2.27	.159	3.66
			15	3.75	.281	11.02
			22.5	4.19	.238	9.83
			30	4.27	.259	11.15
		4	0	1.68	.158	2.64
			7.5	1.82	.117	2.25
			15	2.59	.119	3.12
			22.5	3.61	.168	6.10
			30	4.49	.146	6.58
		5	0	1.39	.101	1.40
			7.5	1.50	.093	1.39
			15	1.70	.110	1.85
			22.5	1.92	.144	2.77
			30	2.33	.116	2.70
Weller	14	1	0	4.93	.300	14.97
			7.5	5.03	.404	20.40
			15	5.28	.366	19.32
			22.5	5.23	.481	25.08
			30	5.18	.499	25.85
		2	0	2.84	.119	3.34
			7.5	3.79	.219	8.33
			15	4.15	.288	12.06
			22.5	4.27	.423	17.79
			30	4.33	.332	14.34

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Weller (cont)	14	3	0	1.33	.195	2.56
			7.5	1.81	.169	3.08
			15	2.72	.242	6.81
			22.5	3.44	.232	7.89
			30	3.38	.246	8.34
		4	0	1.44	.174	2.51
			7.5	1.59	.180	2.95
			15	1.96	.166	3.23
			22.5	2.95	.195	5.86
			30	2.83	.245	6.95
		5	0	1.08	.104	1.11
			7.5	1.37	.084	1.15
			15	1.57	.099	1.55
			22.5	1.96	.084	1.65
			30	1.97	.070	1.38
Monona	6	1	0	4.12	.502	20.60
			7.5	4.17	.515	21.52
			15	4.20	.548	22.98
			22.5	4.33	.565	24.46
			30	4.12	.599	24.71
		2	0	4.09	.166	6.68
			7.5	4.01	.253	10.18
			15	4.16	.299	12.41
			22.5	4.11	.313	12.88
			30	3.98	.378	14.93
		3	0	2.34	.159	3.73
			7.5	3.36	.187	6.28
			15	3.85	.178	6.87
			22.5	4.25	.213	9.08
			30	4.28	.414	17.23

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Monona (cont)	6	4	0	1.19	.146	4.08
			7.5	2.23	.103	2.31
			15	3.14	.116	3.64
			22.5	4.09	.158	5.97
			30	4.70	.158	7.39
		5	0	1.55	.130	2.77
			7.5	1.56	.128	2.00
			15	1.89	.128	2.43
			22.5	2.33	.142	3.32
			30	5.25	.152	8.16
Clarion	17	1	0	2.19	.310	6.76
			7.5	2.30	.437	10.04
			15	2.27	.514	11.58
			22.5	2.25	.522	11.75
			30	2.39	.545	12.94
		2	0	1.08	.071	0.79
			7.5	2.91	.209	6.10
			15	3.11	.300	9.35
			22.5	3.16	.371	11.77
			30	3.16	.314	9.93
		3	0	0.19	.101	0.20
			7.5	1.11	.145	1.61
			15	2.66	.193	5.17
			22.5	3.73	.278	10.33
			30	3.76	.363	13.61
		4	0	0.05	.206	0.11
			7.5	0.27	.139	0.37
			15	1.01	.142	1.39
			22.5	1.98	.159	3.20
			30	2.91	.153	4.25

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Clarion (cont)	17	5	0	0.17	.050	0.09
			7.5	0.17	.091	0.15
			15	0.27	.126	0.89
			22.5	0.94	.094	0.88
			30	1.62	.094	1.52
Webster	18	1	0	2.55	.311	7.91
			7.5	2.39	.445	10.62
			15	2.49	.463	11.48
			22.5	2.58	.486	12.59
			30	2.51	.527	13.27
		2	0	0.98	.082	0.80
			7.5	2.75	.115	2.89
			15	2.88	.148	4.43
			22.5	3.18	.386	12.22
			30	3.20	.420	13.28
		3	0	0.10	.105	0.16
			7.5	0.73	.114	0.84
			15	2.53	.223	5.57
			22.5	3.07	.320	9.80
			30	3.20	.374	11.71
		4	0	0.21	.099	0.20
			7.5	0.19	.170	0.27
			15	0.91	.119	1.09
			22.5	2.15	.139	3.00
			30	3.26	.144	4.68
		5	0	0.27	.109	0.31
			7.5	0.23	.114	0.24
			15	0.44	.079	0.38
			22.5	0.88	.141	1.26
			30	1.47	.105	1.64

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Fayette	20	1	0	2.30	.372	8.52
			7.5	2.44	.417	10.15
			15	2.50	.560	14.00
			22.5	2.46	.502	12.36
			30	2.41	.585	14.11
		2	0	1.17	.121	1.40
			7.5	3.08	.193	5.94
			15	3.41	.319	10.90
			22.5	3.54	.246	8.70
			30	3.50	.325	11.33
		3	0	0.24	.116	0.28
			7.5	1.05	.146	5.17
			15	2.79	.183	5.13
			22.5	3.61	.277	9.93
			30	3.90	.344	13.38
		4	0	0.10	.151	0.10
			7.5	0.16	.212	0.32
			15	0.19	.120	0.63
			22.5	1.67	.134	2.23
			30	2.93	.173	5.08
		5	0	0.14	.328	0.45
			7.5	0.19	.098	0.17
			15	0.25	.102	0.25
			22.5	0.69	.086	0.59
			30	1.37	.113	1.54
Monona	19	1	0	2.86	.369	10.50
			7.5	3.01	.464	13.96
			15	2.97	.473	14.09
			22.5	3.01	.473	14.24
			30	2.99	.469	14.02

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Monona (cont)	19	2	0	2.89	.143	4.08
			7.5	3.45	.237	8.15
			15	3.42	.350	11.98
			22.5	3.45	.429	14.83
			30	3.49	.387	13.58
		3	0	0.96	.122	1.17
			7.5	2.64	.140	3.69
			15	3.63	.217	7.88
			22.5	3.53	.282	9.05
			30	3.70	.361	13.21
		4	0	0.24	.121	0.29
			7.5	0.82	.096	0.79
			15	1.94	.122	2.33
			22.5	3.54	.181	6.37
			30	3.97	.234	9.16
		5	0	0.21	.123	0.25
			7.5	0.32	.099	0.31
			15	0.83	.097	0.95
			22.5	1.75	.104	1.86
			30	3.46	.111	3.87
Weller	21	1	0	2.42	.501	12.13
			7.5	2.31	.493	11.34
			15	2.65	.532	14.09
			22.5	2.65	.565	14.97
			30	2.61	.508	13.25
		2	0	3.43	.202	6.93
			7.5	3.43	.256	8.79
			15	3.50	.283	9.99
			22.5	3.52	.296	10.41
			30	3.56	.327	11.58

Table 42. (Continued)

Soil	Lab. no.	Harvest	Sulfur added ppm S	Dry matter yield g/pot	Percent S %	S yield mg/pot
Weller (cont)	21	3	0	4.06	.327	13.17
			7.5	3.94	.352	13.74
			15	3.86	.367	14.00
			22.5	3.88	.363	13.90
			30	4.18	.359	14.98
		4	0	3.77	.175	6.58
			7.5	3.67	.191	6.98
			15	3.82	.211	8.00
			22.5	4.11	.217	8.92
			30	4.06	.256	10.46
		5	0	3.19	.086	2.70
			7.5	4.27	.097	4.10
			15	4.34	.146	6.43
			22.5	4.70	.192	8.96
			30	4.97	.143	7.06

Table 43. Total dry matter yields on 21 soils and five rates of applied sulfur, summed over five harvests, in Experiment 1/68

Soil	Dry matter yield (g/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Surface soils			
Hamburg	3.25	7.11	10.18	13.36	15.65	9.98
Hagener	3.77	6.46	8.92	11.28	11.97	8.48
Webster	6.87	8.80	11.52	14.09	15.83	11.43
Dorset	6.24	8.15	10.64	12.59	13.61	10.43
Thurman	5.70	7.79	9.70	11.85	14.20	9.77
Sharpsburg	7.73	9.53	12.58	15.91	18.79	12.91
Fayette	7.33	9.05	11.11	13.78	15.40	11.33
Clarion	7.17	9.09	11.36	12.97	15.76	11.27
Tama	7.68	9.95	12.49	14.70	17.39	12.45
Sarpy	9.58	13.00	15.61	17.04	18.53	14.75
Marshall	8.37	10.80	14.26	16.44	18.43	13.66
Grundy	9.40	10.90	13.73	15.43	17.98	13.48
Albaton	11.70	17.95	19.95	20.53	23.49	18.70
Ida	10.50	12.64	15.30	17.28	18.72	14.90
Weller	11.62	13.59	15.68	17.85	17.69	15.29
Monona	13.29	15.33	17.24	19.11	22.33	17.46

Table 43. (Continued)

Soil	Dry matter yield (g/pot) S added (ppm) 0	7.5	15	22.5	30	Mean
			Subsoils			
Clarion	3.68	6.76	9.32	12.06	13.84	9.24
Webster	4.11	6.29	9.25	11.86	13.64	9.04
Fayette	3.95	6.92	9.14	11.97	14.11	9.28
Monona	7.16	10.24	12.79	15.28	17.61	12.62
Weller	16.87	17.62	18.17	18.86	19.38	18.19
Mean surface	8.14	10.62	13.14	15.20	17.24	
Mean subsoil	7.15	9.56	11.73	14.00	15.71	
Mean all soils	7.99	10.40	12.85	14.97	16.87	

Table 44. Dry matter yields, percent sulfur and yield of sulfur in ryegrass, by soils, harvests, sulfur and drying treatment in Experiment 2/68

Soil	Harvest	Sulfur added ppm S	Air-dry treatment[a]	Dry matter yield g/pot	Percent S in ryegrass %	S yield in ryegrass mg/pot
Hamburg	1	0	0	1.42	.092	1.32
			1	2.19	.162	3.55
		5	0	2.59	.212	5.51
			1	3.17	.230	7.29
		10	0	2.75	.267	7.37
			1	2.95	.297	8.77
		15	0	2.61	.293	7.66
			1	3.20	.255	8.14
Sarpy		0	0	2.55	.127	3.24
			1	2.75	.125	3.43
		5	0	3.09	.247	7.65
			1	3.20	.247	7.89
		10	0	3.10	.312	9.51
			1	3.06	.270	8.29
		15	0	3.21	.317	10.20
			1	3.21	.317	10.20
Webster		0	0	2.82	.175	4.94
			1	3.17	.124	3.97
		5	0	3.35	.220	7.39
			1	3.54	.230	8.16
		10	0	3.41	.301	10.30
			1	3.74	.237	8.91

[a]0 = field moist prior to potting; 1 = air-dry prior to potting.

Table 44. (Continued)

Soil	Harvest	Sulfur added ppm S	Air-dry treatment[a]	Dry matter yield g/pot	Percent S in ryegrass %	S yield in ryegrass mg/pot
Webster (cont)		15	0	3.54	.336	11.96
			1	3.69	.322	12.29
Marshall	1	0	0	2.92	.147	4.31
			1	3.25	.162	5.30
		5	0	3.30	.290	9.58
			1	3.43	.250	8.58
		10	0	3.32	.205	6.82
			1	3.46	.280	9.77
		15	0	3.51	.345	12.11
			1	3.59	.310	11.18
Clarion		0	0	2.67	.185	4.95
			1	3.09	.190	5.88
		5	0	3.08	.250	7.76
			1	3.74	.259	9.50
		10	0	3.27	.272	8.87
			1	3.37	.288	9.68
		15	0	3.16	.300	9.48
			1	3.88	.265	10.26
Tama		0	0	3.75	.185	6.97
			1	4.02	.175	7.11
		5	0	3.83	.210	8.02
			1	4.24	.258	10.98
		10	0	3.92	.353	13.85
			1	4.27	.316	13.57

Table 44. (Continued)

Soil	Harvest	Sulfur added ppm S	Air-dry treatment[a]	Dry matter yield g/pot	Percent S in ryegrass %	S yield in ryegrass mg/pot
Tama (cont)		15	0	4.08	.379	15.49
			1	4.55	.322	14.60
Hamburg	2	0	0	0.84	.140	1.18
			1	1.06	.092	0.99
		5	0	1.73	.151	2.61
			1	1.88	.120	2.22
		10	0	3.26	.166	5.41
			1	3.60	.160	5.77
		15	0	3.89	.154	5.99
			1	4.19	.194	8.16
Sarpy		0	0	1.98	.141	2.79
			1	2.26	.106	2.41
		5	0	2.81	.204	5.74
			1	2.95	.203	6.10
		10	0	3.49	.138	4.82
			1	3.54	.198	7.01
		15	0	3.99	.232	9.28
			1	3.99	.250	10.08
Webster		0	0	1.35	.085	1.14
			1	1.58	.118	1.91
		5	0	2.22	.132	2.96
			1	2.46	.154	3.77
		10	0	3.48	.149	5.15
			1	3.60	.144	5.18

Table 44. (Continued)

Soil	Harvest	Sulfur added ppm S	Air-dry treatment[a]	Dry matter yield g/pot	Percent S in ryegrass %	S yield in ryegrass mg/pot
Webster (cont)		15	0	3.96	.216	8.58
			1	4.23	.216	9.16
Marshall	2	0	0	1.64	.111	1.81
			1	1.90	.135	2.61
		5	0	2.47	.122	3.00
			1	2.86	.127	3.71
		10	0	3.74	.176	6.55
			1	3.71	.163	6.03
		15	0	4.58	.197	9.13
			1	4.30	.207	8.97
Clarion		0	0	1.87	.129	2.41
			1	2.22	.159	3.53
		5	0	2.53	.173	4.42
			1	2.81	.152	4.27
		10	0	3.63	.187	6.81
			1	3.91	.194	7.43
		15	0	3.75	.257	9.55
			1	4.03	.189	7.65
Tama		0	0	2.00	.147	2.94
			1	2.51	.157	3.97
		5	0	3.15	.161	5.14
			1	3.39	.141	4.81

Table 44. (Continued)

Soil	Harvest	Sulfur added ppm S	Air-dry treatment[a]	Dry matter yield g/pot	Percent S in ryegrass %	S yield in ryegrass mg/pot
Tama (cont)		10	0	4.09	.126	5.18
			1	4.44	.152	6.77
		15	0	4.33	.218	9.36
			1	4.80	.197	9.52

Table 45. Some chemical characteristics of soils sampled in May, 1969, in Experiment 3/69

Soil	Depth (in)	Moisture content %	Organic carbon %	pH	P pp2m	S ppm
Hamburg	0-6	21.2	1.57	8.2	5	6.0
	6-12	19.0	0.88	8.1	4	3.1
	12-24	18.0	0.45	8.3	4	4.6
	24-36	18.2	0.31	8.4	4	6.6
	36-48	18.2	0.24	8.4	4	6.2
Hagener	0-6	9.6	0.57	7.1	24	2.4
	6-12	11.6	0.79	7.0	23	2.4
	12-24	14.6	0.32	6.6	16	1.7
	24-36	16.8	0.18	6.1	19	2.5
	36-48	18.6	0.17	6.1	21	2.7
Webster	0-6	28.6	3.04	6.6	26	10.3
	6-12	28.7	3.09	6.6	16	7.0
	12-24	26.7	1.10	7.3	8	4.6
	24-36	25.2	0.34	8.2	7	6.3
	36-48	28.6	0.24	8.3	6	7.3
Sharpsburg	0-6	29.0	1.80	7.1	13	5.6
	6-12	27.1	1.19	6.8	10	4.3
	12-24	27.6	0.56	6.7	15	3.8
	24-36	28.8	0.34	6.7	19	2.6
	36-48	26.7	0.25	6.8	23	1.7
Fayette	0-6	29.0	1.16	6.7	27	4.1
	6-12	27.2	0.87	6.7	24	6.4
	12-24	27.6	0.51	6.1	36	5.3
	24-36	28.8	0.33	6.2	38	3.4
	36-48	26.7	0.24	6.3	32	2.3

Table 45. (Continued)

Soil	Depth (in)	Moisture content %	Organic carbon %	pH	P pp2m	S ppm
Clarion	0-6	21.9	2.42	6.6	25	6.8
	6-12	23.0	2.01	6.6	10	5.8
	12-24	22.3	1.37	7.1	6	7.3
	24-36	19.2	0.48	8.2	4	9.4
	36-48	18.5	0.20	8.5	5	6.1